QUALITY ASSURANCE TEST PLAN
FOR A PILOT SCALE WASTE INCINERATION OF NaCN CONTAMINATED FILM CHIPS

Radian Corporation
Research Triangle Park, North Carolina 27709

RADIAN CORPORATION

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Contract No. 68-03-3148
Work Assignment No. 4

November 23, 1983

Approved by:

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Radian QA Officer:		(R. McAllister)
EPA Project Officer:		(D. Oberacker)
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19	Appendix		0	November 23, 1983

List of Copy Holders

1. D. Oberacker, EPA Task Officer
2. D. C. Lewis, CE Raymond
3. W. Kephart, CE Raymond
4. Y. J. Kim, EPA Region V
5. M. O'Toole, EPA Superfund
6. H. O. Chinn, Attorney General's Office, State of Illinois
7. T. Borecki, Attorney General's Office, State of Illinois
8. R. Adams, Radian
9. R. McAllister, Radian
10. M. Hartman, Radian
11. D. Wagoner, Radian

3. PROJECT DESCRIPTION

This document is a test plan for emissions sampling of a pilot scale test involving the incineration of used x-ray film chips which are contaminated with sodium cyanide (NaCN). The purpose of the test is to measure the destruction efficiency (DE) of a rotary kiln and the overall destruction and removal efficiency (DRE) of the complete system equipped with afterburner, quenching and scrubber prior to release of exhaust gases to the atmosphere. The test is to be conducted at CE Raymond test facility in Naperville, Illinois by personnel from Radian Corporation under the guidance of Mr. Oberacker of U.S. EPA from Cincinatti, Ohio.

3.1 BACKGROUND

A quantity of potentially hazardous material consisting of NaCN contaminated shredded x-ray film was discovered by the Illinois State Attorney General's office. There is a total of 16 million pounds of this waste of which the majority 14.5 million pounds contains approximately 500 ppm of NaCN. The Illinois Institute of Technolgy Research Institute (IITRI) was contracted by the State of Illinois to evaluate possible disposal options. It is recommended in a report dated August 31, 1983 that the best action was to burn the cyanide contaminated film chips in a high performance incinerator. EPA/IERL Cinc. and EPA Region V further recommended a pilot scale test to assess the feasibility of incineration prior to a full scale disposal. After a careful search for an available pilot incinerator, the CE Raymond pilot scale rotary kiln with afterburner and scrubber was considered the best available choice. It is located in Naperville, Illinois which is a suburb of Chicago. On October 13 a pre-test visit was conducted at the CE Raymond test facility by Mr. M. Hartman of Radian and Mr. D. Oberacker of U.S. EPA/Cincinnati to obtain information necessary for the preparation of this report.

3.2 FEED MATERIAL INFORMATION

During the pre-test visit Radian obtained a sample of the contaminated x-ray film chips and they were analyzed to verify the reported contaminants of the film. The reported analysis of the film is listed in Table 3-1. The film chips consist of shredded thin film layers of ¼ to ½ inch in diameter. They are covered with a wetness of the last rinse liquid that was used during the recovery of the silver content of the film. Analysis of the chips obtained during the presurvey performed on November 22, 1983 by Radian reported 800 ppm NaCN.

Table 3-1. PREVIOUS ANALYSIS OF CONTAMINATED FILM CHIPS

Polyester	~ 70%[a]
Acetate	~ 30%
Silver (Ag)	96 ppm
NaCN	300 - 500 ppm
Mercury (Hg)	Trace (i.e., <10 ppm)
Lead (Pb)	Trace
Zinc (Zn)	Trace

[a]Analysis of the market for detoxified film chips.

IITRI Project PO 8419, August 1983.

3.3 DESCRIPTION OF PROCESS

Rotary Kiln
- capable of 2,700°F max
- ~.68 second retention time @ 2,200°F
- Dimensions 18" ID x 15' length
- counter current burner when auxilliary fuel used

Transition Duct
- 12" ID x 10' length (mostly horizontal)
- ports at 4 DIAs and 2 DIAs
- additional retention time ~0.3 second

After Burner	• capable of 2,400°F max • ∿3.9 second retention time @ 2,200°F • dimensions 5' ID x 8' length
After Burner Transition Duct	• 18" ID x 16' long (mostly verticle) • additional retention time ∿.7 second • ports located ideally at 8 DIAs and 2 DIAs
Quench System	• spray water system • cooling H_2O added in quantities to minimize the quench water out
Venturi Scrubber	• 20" - 40" pressure drop • recirculating scrubber water • cyclonic demister
ID Fan	• normally rated 440 SCFM
Exhaust Stack	• ports to be placed at 8 DIAs and 2 DIAs

3.4 COMBUSTION CALCULATION

Feed - 50 #/hr feed @ 500 ppm NaCN = 11.32 grams/hr feed or 0.189 gr/min.

Flow = 440 DSCFM exhaust flow.

CASE 1 - 0% Destruction

0.189 gr/min ÷ 440 DSCFM = 0.43 mg/SCF

or (5.6 ppm NaCN in the exhaust gas)

CASE 2 - 99.999% Destruction Efficiency

90 ft^3 sample - 4 hour test

0.43 mg/DSCF x 90 DSCF x .00001 = <u>0.39 µg/sample</u>

Assume 200 mL in impingers of the sampling train.

Minimum detectable in method =

<u>colorimetric</u> ⟶ 20 µg/liter

or 4 µg/sample taken.

To Seed ———→ 1% level = 10,000 ppm.

CASE 1 - 0% Destruction

3.78 gr/min ÷ 440 DSCFM = 8.59 mg/SCF
or (112.6 ppm NaCN in the exhaust gas)

CASE 2 - 99.999% Destruction

90 ft^3 sample - 4 hour test

8.59 x 90 x .00001 = 7.73 µg/sample

CASE 3 - 99.99% Destruction

8.59 x 90 x .0001 = 77.3 µg/sample

CASE 4 - 99.9% Destruction

8.59 x 90 x .001 = 773 µg/sample
or (.1 ppm NaCN in the exhaust gas)

3.5 FEED INFORMATION

The chips found are in various conditions. The proposed type of sample would be the worst case of chips which are contaminated with the last rinse of recovery and which contain ~500 ppm of NaCN. The following options are available for the feeding of the contaminated chips.

a) Straight feed of chips via the CE feed gun.
b) Seeded chips (i.e., chips with 10,000 ppm NaCN) fed straight to the kiln.
c) Bagged or prepackaged chips to simulate a full scale burn.

Both options b and c involve an increased handling of the contaminated chips. During Phase I of the test plan some of the feed problems could be resolved as well as a method to measure the feed rate.

4. PROJECT ORGANIZATION AND RESPONSIBILITY

The primary responsibilities and supporting roles of each member of the project team are summarized in Figure 4-1. Project Manager, Mr. R. C. Adams, has the ultimate responsibility and authority for the entire project. He will provide overall technical and administrative supervision of all project aspects, and will be assisted by the appropriate personnel who will perform administrative tasks such as cost performance and scheduling. He will be the principal point of contact with EPA and CE Raymond.

Frequent contacts as needed between Mr. Adams and the EPA, supplemented with monthly technical progress reports, will provide EPA personnel with ongoing current information regarding the progress and anticipated problems. Mr. Adams will notify the EPA project officer if a significant problem is anticipated (a significant problem is one which may affect technical performance, schedule, or cost, either short-term or long-term).

The program's QA activities will be directed by the QA Officer, Dr. R. A. McAllister. Dr. McAllister will report directly to the Project Manager as shown in the project organization chart, Figure 4-1. He will select quality monitors for different aspects of the project. He will have full authority to coordinate, direct, and administer all QA activities as depicted in Figure 4-2. This is a functional diagram for QA, and will cover all project activities and serve as a master planning and control document. He will also serve as a technical advisor to give solicited and unsolicited advice, and will make recommendations to the Project Manager.

The QA Officer will coordinate the activities of the Quality Control and Technical Advisory Group (QC/TA). The purpose of this group will be to review test plans for sampling and analysis, make recommendations for

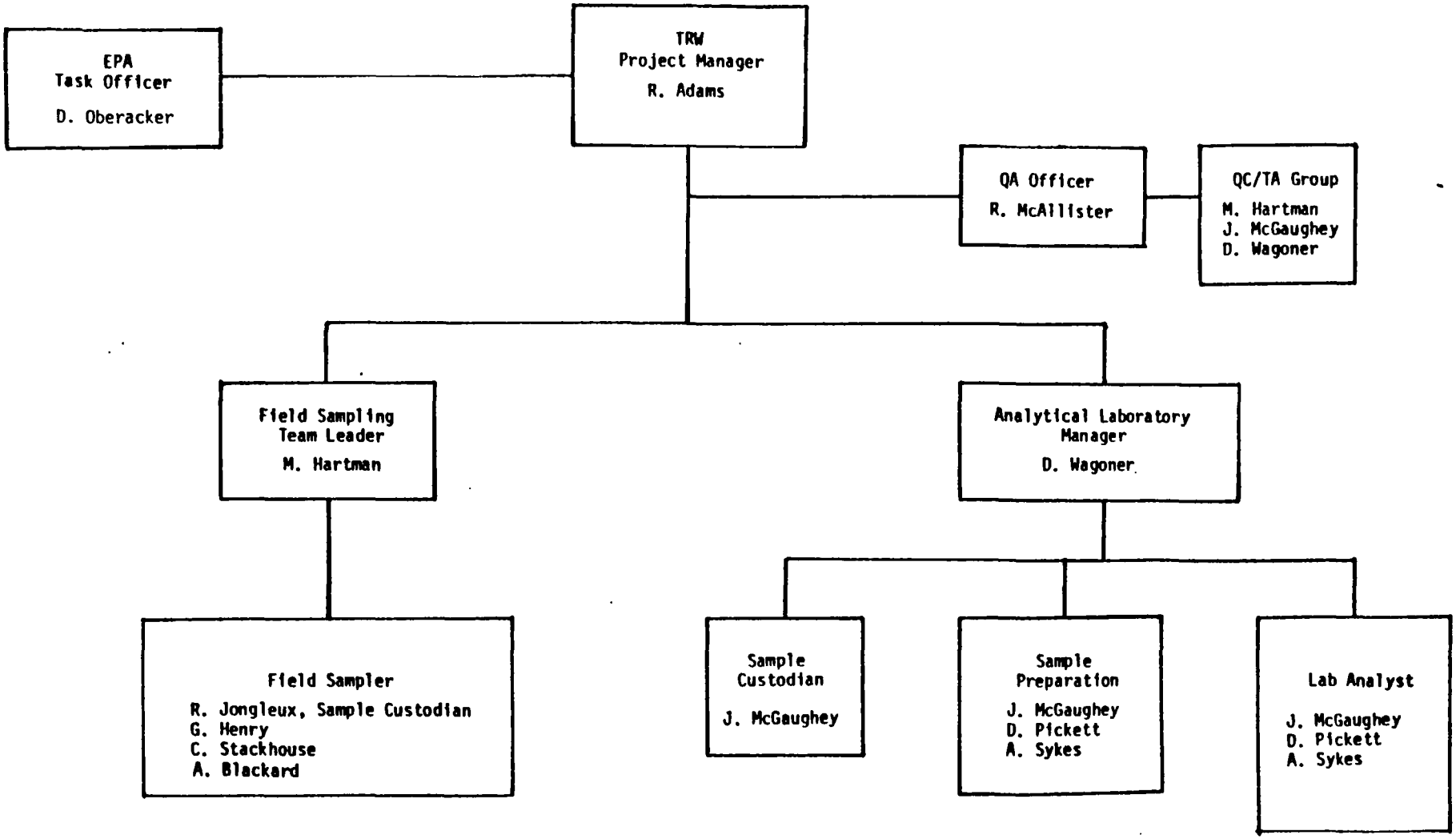


Figure 4-1. TRW project organization.

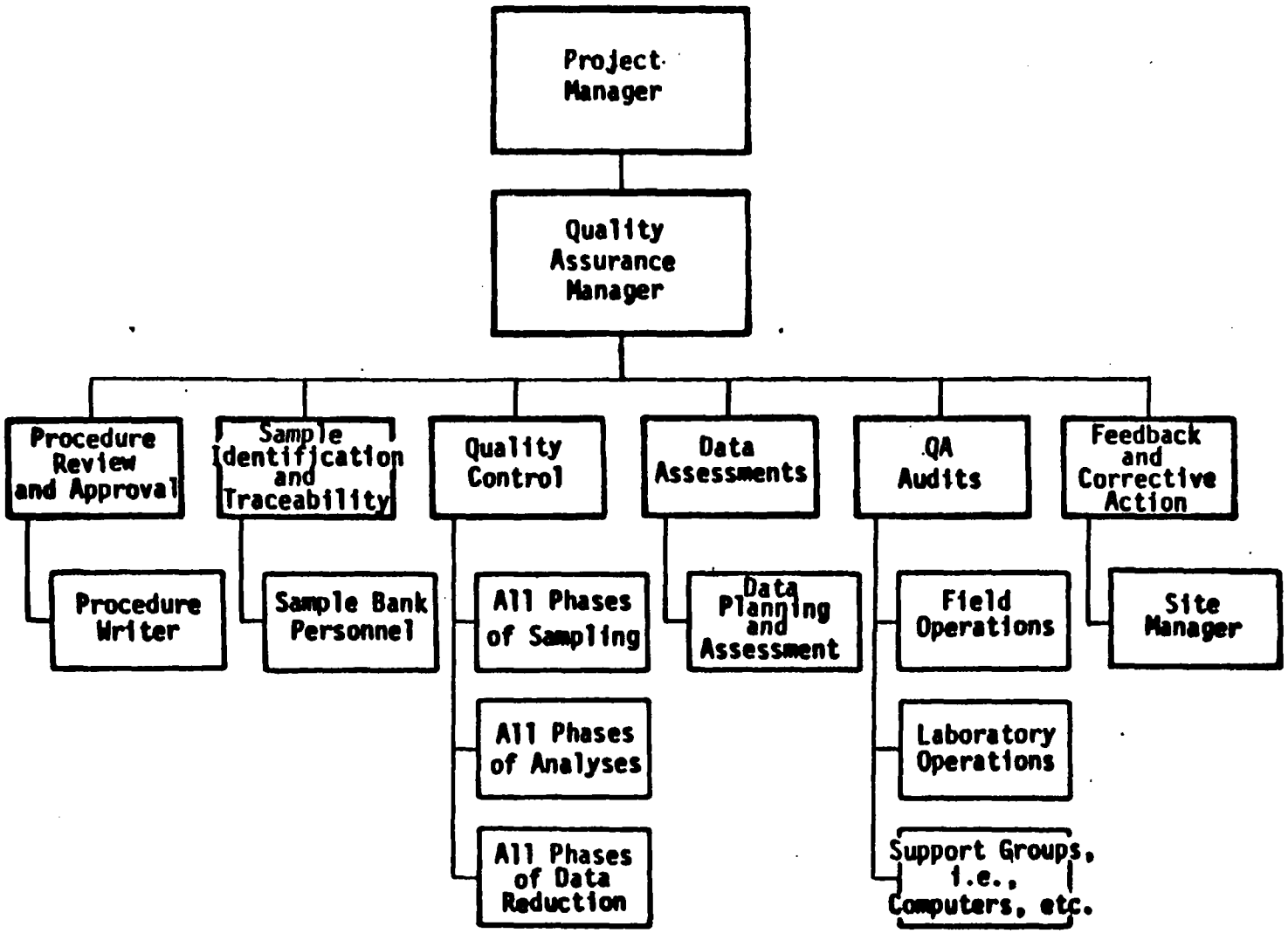


Figure 4-2. Functional diagram for quality assurance.

alternate test approaches, assist in resolving problems, review and carry out QA plans, and review collected data.

The Field Sampling Team Leader has the responsibility to ensure that the test procedures are conducted in a timely and accurate manner. His responsibility is to be sure that the tests are performed according to the procedures specified. The Field Sampling Team Leader reports daily to the Project Manager and relays to him on a timely basis the overall progress and/or problems or potential problems.

The Sample Custodian is responsible for keeping a log of all the samples taken each day. He makes sure each sample is properly labeled, identified, and packed for shipment to the Radian Research Triangle Park analytical laboratory. A Sample Custodian will be appointed in the laboratory to handle incoming samples from the field activities.

A quality control monitor will be selected for each set of activities and identified in the daily log of the Project Manager. The role primarily addresses internal audits of sampling and analysis procedures. A description of the tasks to be done and the responsibilities of the quality control monitor are detailed in Section 12.

The Radian laboratory facilities, located at Research Triangle Park, North Carolina, will be responsible for performing the analyses that are provided below. The preparation and/or dispensing of audit materials will be conducted through the Research Triangle Park laboratory under the direction of the QA Officer.

The lines of communication between management, the QC/TA group, the technical staff, and within the technical staff are established and will allow for mandatory discussions of resulting problems, potential problems, preventive actions, and corrective procedures.

The major quality control responsibilities and quality assurance review functions are summarized below:

Performance	Major Quality Control Responsibility	Primary Quality Assurance Review
1. Project Manager	• Procedure Change Approval	QA Office
	• Response to Compliance Failures	QA Office
	• Information Completeness Check	QA Office
	• Information Validity Review	QA Office

Performance	Major Quality Control Responsibility	Primary Quality Assurance Review
2. Quality Assurance Officer	• Procedure Approval	Project Manager
	• Test Plan Approval	Project Manager
	• Quality Anomaly Recommendations	Project Manager
	• Quality Reports	Project Manager
3. Field Sampling Manager or Laboratory Manager	• Equipment Downtime Record	QA Office
	• Information Validity Review	Quality Monitor
	• Information Completeness Check	Quality Monitor
	• Procedure Currentness	Quality Monitor
	• Response to Completeness Check Failures	QA Office
4. Field Sampling Team Leader	• Preventive Maintenance	Project Manager
	• Documentation	Project Manager
	• Sample Integrity	Quality Monitor
	• Calibration and Procedures	Quality Monitor
5. Sample Custodian	• Information Completeness Count	Quality Monitor
	• Documentation	Field Sampling Team Leader
	• Sample Integrity	Quality Monitor
	• Inventory Crosscheck	Field Sampling Team Leader
6. Sample Preparation	• Information Completeness Count	Quality Monitor
	• Sample Integrity	Quality Monitor
	• Documentation	Field Sampling Team Leader
	• Procedures	Quality Monitor
	• Test Blanks	Field Sampling Team Leader
7. Quality Monitor	• Performance Audit	Quality Assurance Officer

5. QUALITY OBJECTIVES

The major quality objective of this project plan is to provide a practical means to implement quality assurance techniques into a program involving the destruction and removal efficiency of NaCN waste in a rotary kiln incinerator. An objective of this program is to devise and select testing procedures that are simple and direct, but that measure the destruction and removal efficiency for the components of interest when the waste is incinerated.

In order to facilitate the following discussion, it is useful to define the following three terms; namely data quality, quality control, and quality assurance.

1. Data Quality: The totality of features and characteristics of a product (measurement data) that bears on its ability to satisfy a given purpose. These characteristics are defined as follows:

- Accuracy – The degree of agreement of a measurement (or an average of measurements of the same thing), X, with an accepted reference or true value, T, usually expressed as the difference between two values, X-T, or the difference as a percentage of the reference or true value, 100 (X-T)/T, and sometimes expressed as a ratio, X/T. Accuracy is a measure of the bias in a system.

- Precision – A measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation (or the relative standard deviation). Various measures of precision exist depending upon the "prescribed conditions."

- Completeness – A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions.

- Representativeness – The degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition.

- Comparability – A measure of the confidence with which one data set can be compared to another.

2. Quality Control: The overall system of activities whose purpose is to provide a quality product or service; for example, the routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process.

3. Quality Assurance: A system of activities whose purpose is to provide assurance that the overall quality control is in fact being done effectively.

- The total integrated program for assuring the reliability of monitoring and measurement data.

- A system for integrating the quality planning, quality assessment, and quality improvement efforts of various groups in an organization to enable operations to meet user requirements at an economical level. In pollution measurement systems, quality assurance is concerned with the activities that have an important effect on the quality of the pollutant measurements, as well as the establishment of methods and techniques to measure the quality of the pollution measurements. The more authoritative usages differentiate between "quality assurance" and "quality control," where quality assurance is the "system of activities to provide assurance that the quality control system is performing adequately."

In summation, the purpose of QA is to assess independently the overall QC program. This assessment of QC is done in two ways. Reviews and performance audits are conducted by the QC organization itself (in internal assessment program), and in additional periodic assessments by an independent outside organization.

It is required for a thorough data quality program to delineate the quality elements for the organization and the required measurement program. This quality assurance plan will include provisions for the following elements:

1. the use of validated, well conceived analytical test methods and well constructed, equipped, and maintained laboratory facilities;

2. collection of representative samples;

3. use of high quality glassware, solvents, and other testing materials;

4. scheduled, periodic calibration, adjustment, and maintenance of equipment;

5. use of control samples and standards;

6. strict adherence to analytical procedures;

7. internal and external review of methods and results;

8. internal and external proficiency testing;

9. use of replicate samples;

10. open lines of communications between management and test personnel;

11. data validation and review;

12. data storage and retrieval;

13. up-to-date sample log and instrument maintenance and calibration records; and

14. periodic review of current, pertinent literature.

5.1 PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES

Quantitative guidelines for precision, accuracy, and completeness objectives have not been established for trial burns. Composition measurements from continuous monitors can be made with precisions of ±5% and accuracies of ±10% according to 40 CFR 60 Appendix A.

Completeness objectives of all measurements can be set at 90%.

Process measurements will be made by AWWU. Radian will estimate instrument precisions based on the specifications of these devices. These include incinerator temperature and waste oil flow and scrubber water flow sensors. AWWU is requested to calibrate the temperature transmitters and flow meters just prior to testing and to supply TRW with the calibration records. The method for determining sludge feed rate and weight of dry solids have no quantitative guidelines for precision, accuracy, and completeness objectives. AWWU will minimize measurement error to the extent possible by following these procedures:

1. Verify filter speed of revolution by manual observation.

2. Describe in detail the procedure for sampling each filter cake. Report dimensions of sample to the nearest 0.1 inch and weight of sample in grams to one decimal place.

3. Describe in detail the analytical procedure. Provide detailed calculations for determining sludge feed rate.

4. Report all information to Radian.

Ultmate/proximate analyses will utilize ASTM Methods D2015, D3173, and D3176. Precision guidelines are inherent in these methods. Radian will review the results from the analysis of sludge for completeness and for compliance with precision requirements.

6. SAMPLING PLAN

A three-phase approach to the sampling of the gaseous emissions resulting from the combustion of the contaminated film chips has been proposed. The three phases are as follows.

Phase I - a demonstration burn of "clean" film chips to familiarize the CE staff with the feeding and burning requirements of the chips and the kiln. No gaseous samples or feed samples are to be taken during this phase.

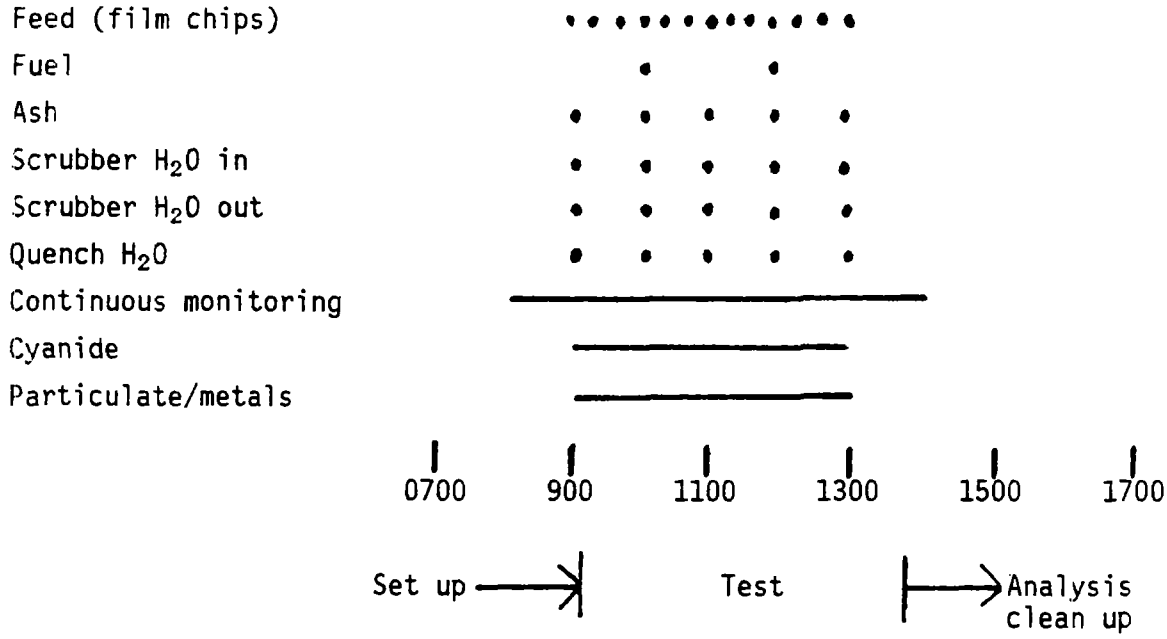
Phase II - three investigation burns to establish the set points for the Phase III trial burn. The burns will be conducted at three differing kiln temperatures with the afterburner temperature fixed at a high level. Gaseous, liquid and feed and ash solid samples are to be taken by TRW. (SCA temperatures for the typical burner at full scale are in 1,600-1,800°F range.)[1]

Table 6-1. PHASE II KILN AND AFTERBURNER SET POINTS

Kiln temperature	Afterburner temperature
2,000°F	2,192-2,300°F (1,200-1,260°C)
1,700°F	2,192-2,300°F (1,200-1,260°C)
1,300°F	2,192-2,300°F (1,200-1,260°C)

- all samples during Phase II to be conducted over ~ 2.5 hour period (see Table 6-2)

Table 6-2. DAILY SAMPLING SCHEDULE



		Test conditions
Day 1	Equipment preparation	
		Kiln/Afterburner
Day 2	Test 1 Phase II	2,000°F/2,300°
Day 3	Test 2 Phase II	1,700°F/2,300°
Day 4	Test 3 Phase II	1,300°F/2,300°
Day 5	Test 1 Phase III	@ temperatures
Day 6	Test 2 Phase III	determined in
Day 8	Equipment dismantle	Phase II

Phase III - trial burn. Two duplicate runs at a kiln temperature determined by the investigation phase (e.g., 1,700 kiln 2,192°F afterburner). The samples are to be obtained over two separate 2.5 hour periods.

6.1 SAMPLING POINTS

Figure 6-1 presents a schematic drawing of the combustion process and the associated control equipment. Indicated on this figure are the three proposed sample points of a gaseous monitoring. Also indicated are the six sample points where process samples are to be taken. Continuous combustion/emission monitoring will be conducted on the outlet of both the kiln and the afterburner (points 1 and 2). In addition to these samples of the combustion process, an ambient air monitor for HCN will be located in the proximity of the two combustion chambers. This device will be maintained primarily as a safety precaution but also to detect any leaks in the system which may affect the gaseous measurements. The alarm limit of this instrument is 10 ppm of HCN*.

6.2 SAMPLING MATRIX

Table 6-3 indicates the samples to be taken from the various sample points, the frequency of sampling, minimum volumes, and the analysis to be performed. All of these samples/measurements are to be taken during each of the six burns conducted during Phases II and III. The continuous monitors for O_2, CO_2, CO, NO_x, and total hydrocarbon (THC) are to be supplied from point 1 and point 2 in alternating five minute periods. These monitors will be used to monitor the combustion efficiency, excess air and emission levels after both combustion chambers. The test plan calls for alternating between the kiln outlet and the afterburner outlet every five minutes; however, if instability due to response time, memory effects or changes in concentration are encountered. The sample switching can be extended to every 10 minutes.

Cyanide sampling with the gaseous monitoring apparatus (modified NIOSH train) will be conducted for analysis of particulate sodium cyanide and HCN gas or free CN from sample points 1, 2 and 3. These samples will be taken isokinetically from the sample ducts over a four hour

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*OSHA limit.

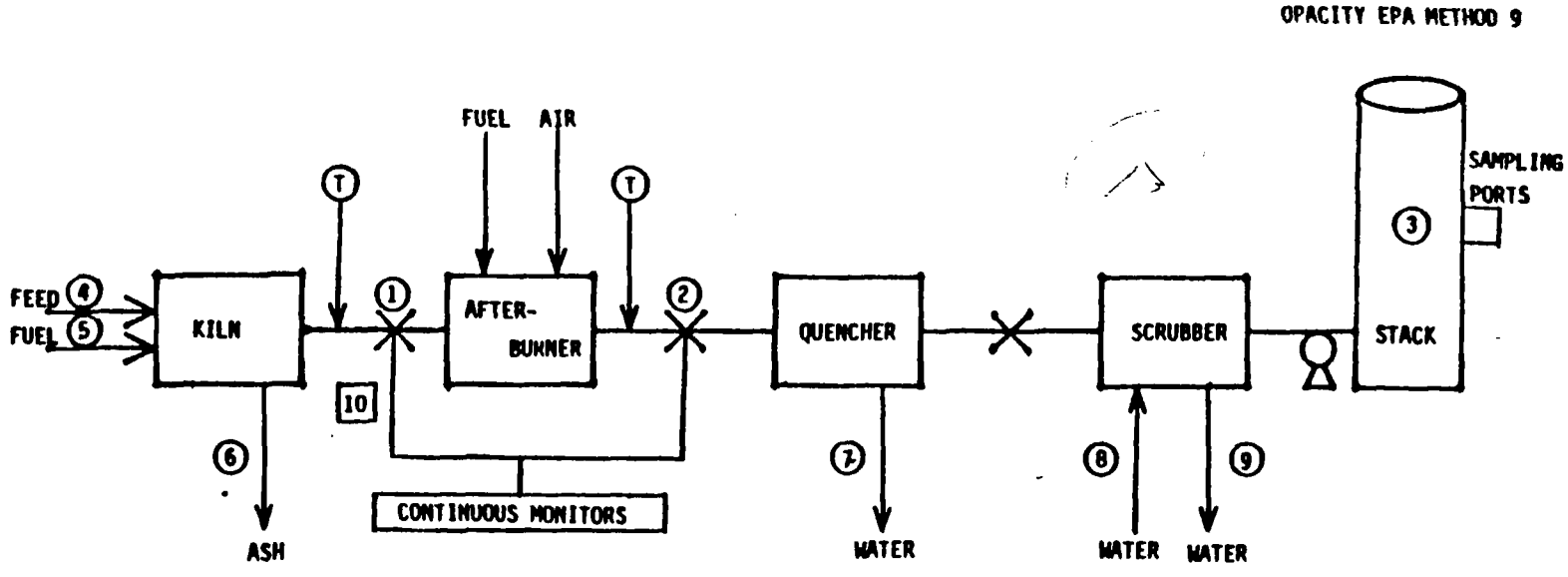


Figure 6-1. Sample locations.

Table 6-3. SAMPLES/MEASUREMENTS TO BE TAKEN FOR EACH BURN

Parameter	Frequency/volume	Analysis method
Combustion/Emission Parameters (sample points 1 and 2)		
O_2	continuous*	Paramagnetic
CO_2	continuous*	Infrared
CO	continuous*	Infrared
NO_x	continuous	Chemiluminescent
THC	continuous	Flame ionization
T	continuous	
Manual Sampling		
Cyanide	1-4 hour test/burn from sample points 1, 2, 3. Min 90 ft^3 plus 1 blank per phase.	Particulate CN from membrane filter HCN in NaOH solution. Selective ion electrode/ colorimetric.
Particulate	1-4 hour test/burn from sample point 3 only. Min 90 ft^3 plus 1 blank per phase.	Gravimetric for particulate. A.A. for metal analysis of Ag, Hg, Zn, Pb, Na, Cd, Ni, Cu, Fe.
Feed/Process Stream Sampling		
Fuel gas sample	2/burn if used. One liter each.	CN
Contaminated film feed	Every 10 minutes for 4 hours - composited for each hour of burn. 100 grams/ sample. Total 1,200 grams/test.	NaCn + HCN + "CN^-"
Ash	Every hour of test 100 grams each to be composited to 1 composite of 500 grams total	A.A. or ICAP for metal analysis of Cn, Ag, Hg, Zn, Pb, Na, Cd, Ni, Cu, Fe
Scrubber H_2O inlet and outlet	1 liter every hour of testing. ½ liter to be composited after 2 liters for each 4 hour test	CN
Quench H_2O	Same as above	CN

*Kiln outlet and afterburner outlet will be alternated every five minutes during normal testing.

period. The analysis will be conducted onsite in the Radian mobile laboratory immediately following the test by a Radian chemist. A minimum of 90 dry standard cubic feet (DSCF) will be sampled during each test. The filter will be analyzed separately from the impinger catch to differentiate between particulate cyanide and gaseous cyanide.

The process samples will be taken according to the schedule presented in Table 6-2. The water samples will be analyzed in the mobile laboratory immediately following collection. The ash, feed and fuel gas samples will be transported to the TRW laboratory at Research Triangle Park, NC for analysis. The scrubber water will be analyzed each hour and then at the end of the test on the composite. A decision will be made during the investigation phase as to which set of samples (individual or composite) to analyze during the trial phase.

6.3 SAMPLING PROCEDURES

This section contains a brief description of the sampling procedures to be followed during Phase II and Phase III of the test burn.

6.3.1 Cyanide Sampling

The gaseous cyanide sampling will be conducted utilizing the principle described in the NIOSH S250 sampling method with the following modifications.

- The cellulose membrane filter will be replaced by a glass fiber filter.
- The midget impinger will be replaced by a series of standard Greenburg-Smith impingers.
- Each of three impingers will contain 100 ml of 0.1 NaOH
- The sampling apparatus will be run as described in EPA Method 5.

The NIOSH method number S250 is contained in its entirety in the Appendix of this report as is the EPA Waste Water Method 00720 from EPA 625/6-74-003a Methods for Chemical Analysis of Water and Wastes.

The probes will be quartz-lined water cooled except at sample point 3 which will be a glass-lined heated probe. In all other respects they will conform to EPA Method 5. The samples will be extracted isokinetically with the flows, temperatures, meter volume and impinger conditions monitored. The filters will be weighed gravimetrically and subsequently saved for analysis of cyanide. The impinger contents will be analyzed separately for cyanide.

6.3.2 Metals Analysis

A separate sampling train will be run in accordance with EPA Method 5 with the filter saved for analysis by A.A. for metals. The train will be operated in accordance with Method 5 except that water cooled quartz-lined probes will be utilized at sampling points 1 and 2.

6.3.3 Continuous Monitoring

Sample points 1 and 2 will be monitored semi-continuously for O_2, CO, CO_2, NO_x and THC (see Figure 6-1). A heated (120°C) sample line will be connected to each sample port with an instack scintered metal filter. The sample lines will be connected to a three-way valve that will be used to select the sample position to be analyzed. A time period of five minutes sampled at each point has been selected; however, if this proves to be insufficient the time period may be lengthened. The sample selected will split prior to a gas conditioner and an approximate flow of four liters per minute will be delivered to the THC analyzer (Beckman 402 flame ionization detector). This occurs in order not to condense hydrocarbons with the moisture removal system that is necessary for the other analysers. Since the water vapor content of the sample gas will be above the practical limits for some of the continuous gas monitors, a sample gas conditioner will be utilized to condense and remove the moisture and thus provide a dry gas stream for the CO, O_2, CO_2, and NO_x gas monitors. The total hydrocarbon analyzer uses untreated stack gas, thus giving an analysis on a wet basis as seen in Figure 6-2.

The sample gas will be pumped into a glass sample manifold at a flow rate which exceeds the total sample requirements of the individual gas monitors. The common sampling manifold will, therefore, offer slipstream sample flows to each monitor. Maintaining excess sample flow ensures that there are no measurement errors due to back dilution from ambient air. Also, since the sampling manifold is exhausted to ambient pressure the manifold itself remains at ambient pressure and eliminates measurement errors which could arise from varying stack pressures and pressure effects which could be caused by interaction between the individual sample pumps of the gas monitors.

To ensure representative measurements, all gases for calibration will be introduced through the heated sampling line such that it follows

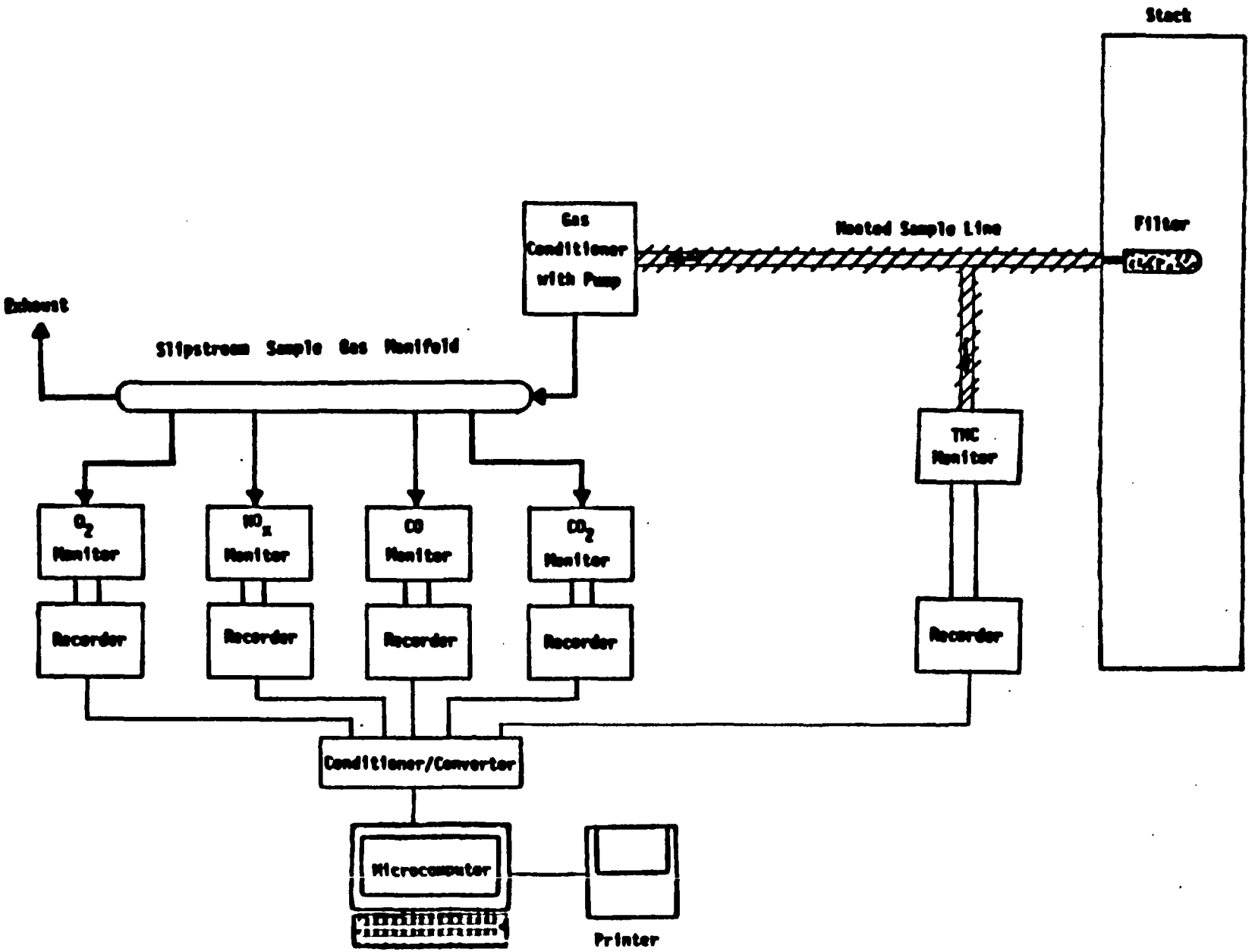


Figure 6-2. Continuous monitoring and data collection.

the same flow path as actual sample gas. The heat-traced sample line will be attached in such a manner that it can be removed to introduce calibration gases or shifted to the stack probe.

6.4.1 Analytical System

The continuous monitors will indicate the profiles of the following stack gas constituents over the course of the test: oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), oxides of nitrogen (NO_x), and total hydrocarbons (THC). Oxygen in the sample gas will be detected on a dry basis by a gas monitor which employs paramagnetic detection of the oxygen molecule directly. Carbon dioxide and carbon monoxide will be measured on a dry basis using monitors which measure the respective species by infrared absorption at a characteristic wavelength using a non-dispersive infrared instrument (NDIR).

The total oxides of nitrogen (NO_x) will be quantified on a dry basis by an analyzer which first converts all of the nitrogen oxides present in the sample to nitric oxide which then reacts with a self-generated ozone stream. Detection of the distinctive chemiluminescent wavelength of this reaction yields a measure of the total oxides of nitrogen. The total hydrocarbon content of stack gas will be measured on a wet basis with a heated flame ionization detection (FID) analyzer to give a measure of the overall hydrocarbon emissions. The data from all of the above mentioned continuous monitors can be corrected using the moisture data from the coinciding EPA Method 5 testing to show the actual stack gas composition on a wet basis.

6.3.4 Liquid Samples

All samples are to be withdrawn from a point or area which will provide the most representative sample possible. A flowing stream containing particulate or insoluble phases will be stratified. The optimum sampling location will, therefore, be located after a bend where turbulent mixing will induce homogeneity. In all cases, the main pipe or stream flow must be sampled. Because solids can accumulate in seldom used vent or slipstreams, these lines are not recommended for sample acquisition.

To acquire the tap sample of the scrubber and quency water, the valve or stopcock used for sample removal must be fitted with a length

of precleaned Teflon® tubing long enough to reach the bottom of the sample container. Because of the wide diversity in valve and stopcock nozzle sizes, a full range of male-to-female and female-to-male Teflon® or stainless steel tube adapters are required. A piece of Teflon® tubing of sufficient length to reach to the bottom of the sample container is coupled to the appropriate male or female adapter. The adapter is then coupled to the valve or stopcock.

The sample is removed by a stopcock or valve by inserting a clean Teflon® line into the sampling bottle so that it touches the bottom. The sample bottle should be thoroughly rinsed with sample prior to filling. The sample line flow must be regulated so it does not exceed 500 mL/min after the sample line has been flushed at a rate high enough to remove all sediment and gas pockets. The apparatus used for tap sampling is illustrated in Figure 6-3. If sampling valves or stopcocks are not available, samples may be taken from water-level or gauge-glass drain lines or petcocks.

Caution must be exercised while sampling with this technique. The valve must be cracked slowly to allow for escaping air pockets, and to prevent injury due to toxic or heated streams.

6.3.5 Feed Sampling

The preferred method of feeding the contaminated film chips is to prepackage them in cardboard or plastic containers and to feed them sequentially into the kiln. The sampling will consist of taking samples of each container and compositing these chips into an hourly sample. Each hourly sample will be sealed and shipped to the RTP laboratory for analysis.

6.3.6 Fuel Samples

Fuel samples will be taken once per test and analyzed for cyanide content. These sample will be taken in the same manner as the liquid samples, sealed in a shipping container and transported to the RTP laboratory for analysis.

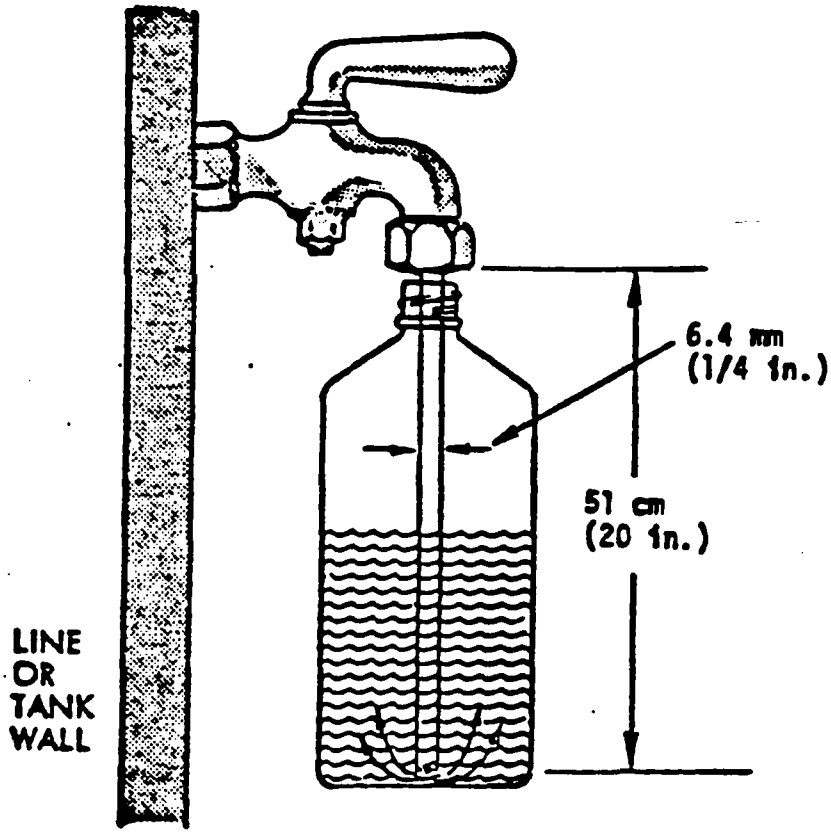


Figure 6-3. Assembly for tap sampling.

7. SAMPLE CUSTODY

This section provides the quality control requirements associated with custody of samples taken in this project, including both field custody and subsequent laboratory custody actions. A set of general QC requirements is also presented for use by all sample custodians. For the purposes of these requirements, a custodian is considered any person designated to provide receiving inspection, physical acceptance of a group of samples intended for subsequent treatment or analysis, analysis tracking, or sample repository operation. An important QC activity performed by the custodian is completeness checking of records, data, identities etc., of the samples, primarily with respect to a preplanned sample inventory.

7.1 GENERAL REQUIREMENTS

All custodians in this program are required to present plans for maintaining custody, sample integrity, and adequate records of all test samples. A plan will identify:

- Name of sample custodian(s)
- Laboratory tracking report sheets to be used which identify
  - Sample code number, reserve sample, quantity, aliquot for each test, responsible person, date received, date completed
  - Storage facility for reserve samples
  - Method for using hard-bound workbooks in conjunction with lab tracking report sheets to note unusual events
  - Quality control inspection results on incoming samples
  - Method of identifying sample at any stage of testing, using existing laboratory practices
- Use of the completeness check as described in Section 7.4.

7.2 FIELD CUSTODY

To ensure the integrity of collected samples, and to maintain a timely and traceable transfer of samples, an established and proven chain of custody or possession is mandatory. It is imperative that accurate records be maintained whenever samples are collected, transferred, stored, analyzed, or destroyed.

The primary objective of these procedures is to create an accurate written record that can be used to trace the possession of the sample from the moment of its collection through the reporting of the final results. A sample is in custody if it is in any one of the following states:

a. In actual physical possession
b. In view, after being in physical possession
c. In physical possession and locked up so that no one can tamper with it
d. In a secured area, restricted to authorized personnel.

Personnel will receive copies of study plans prior to the study. Prestudy briefings should then be held to apprise participants of the objectives, sample locations, and chain-of-custody procedures to be followed. After the chain-of-custody samples are collected, a debriefing is held in the field to verify the adherence to the chain-of-custody procedures and to determine whether additional samples are required.

The personnel involved with the sampling and analyses effort will be briefed by the Project Manager in regard to the following rules.

a. Involve a minimum number of trained persons in sample collection and handling.
b. Establish guidelines for particular procedures to be used for each type of sample collection, preservation, and handling.
c. Minimum handling of samples.
d. Obtain samples using the appropriate sampling techniques.
e. Attach sample tag or label securely (see Figure 7-1) to the sample container at the time the sample is collected. The label will contain the following items as a minimum: the station number and location, the date and time taken, the type

DATE _____

SAMPLE NUMBER _____

TYPE SAMPLE _____

FRACTION _____

COMMENTS _____

COLLECTED BY _____

SOURCE I.D. _____

Figure 7-1. Example of sample label.

of sample, the sequence number (e.g., first sample of the day-sequence No. 1), the preservative used (if any) and the name of the sample collector. Labels will be completed legibly in waterproof ink. The samples will be sealed to preserve the integrity of the sample from the time it is collected until it is opened in the laboratory.

f. Use bound field notebooks to record field measurements and other pertinent information necessary to reconstruct the sample collection processes for future reference. Maintain a separate set of field notebooks for each study and store them in a safe place where they can be protected and accounted for at all times. Establish a sample log sheet with a standard format to minimize field entries and include the serial number of the sheet, the date, time, survey, type of samples taken, volume of each sample, type of analyses, unique sample numbers, sampling location, field measurements and any other pertinent information or observation. The QA Manager will be responsible for the preparation of the necessary sample log sheets, etc., and the periodic review of all notebooks during and after the study. The Project Manager will be responsible for the safe keeping of all notebooks at completion of the project. The entries should be signed by the sample collector.

g. The sample collector is responsible for the care and custody of the samples until the samples are properly dispatched to the receiving laboratory or given to an assigned custodian. The sample collector will insure that each container is in his physical possession or in his view at all times, or stored in a locked place where no one can tamper with it.

In the transfer-of-custody procedures, each custodian or sampler will sign, record, and date the transfer. Sample transfer can be a sample-by-sample basis or on a bulk basis. The following protocol will be followed for all samples as they are collected and prepared for distribution.

a. Samples will be accompanied by a chain-of-custody record (Figure 7-2) that includes the name of the study, collectors' signatures, station number, station location, date, time, type of sample, sequence number, number of containers, and analyses required. When turning over possession of samples, the transferor and transferee will sign, date, and time the record sheet. This record sheet allows transfer of custody of a group of samples in the field to the mobile laboratory or to the central laboratory.

b. If the custodian has not been assigned, the field custodian or field sampler has the responsibility of packaging and dispatching samples to the laboratory for analysis. The appropriate chain-of-custody record must be filled out, dated, signed, and included with the sample. A copy will remain with the custodian.

c. To avoid breakage, samples will be carefully packed in shipment containers such as ice chests. The shipping containers will be sealed for shipment to the receiving laboratory.

d. Packages must be accompanied by the chain-of-custody record showing identification of the contents. The original must accompany the shipment. A copy is retained by the Field Sampling Team Leader.

e. If sent by mail, register the package with return receipt requested. If sent by common carrier, a bill of lading should be obtained. Receipts from post offices and bills of lading will be retained as part of the permanent chain-of-custody documentation.

f. If delivered to the laboratory when appropriate personnel are not there to receive them, the samples must be locked in a designated area within the laboratory or must be placed in a secure area, so that no one can tamper with them. The recipient must return to the laboratory, unlock the samples, and deliver custody to the appropriate custodian.

Collector's Sample No. _____
_____
_____
_____

CHAIN OF CUSTODY RECORD

Location of Sampling: _____ Producer _____ Hauler _____ Disposal Site
_____ Other: _____

Sample

Shipper Name: _____

Address: _____
number street city state zip

Collector's Name _____ Telephone: (___) _____
signature

Date Sampled _____ Time Sampled _____ hours _____

Type of Process Producing Waste _____

Field Information _____

_____

_____

Sample Receiver:

1. _____
name and address of organization receiving sample

2. _____

3. _____

Chain of Possession:

1. _____ _____ _____
signature title inclusive dates

2. _____ _____ _____
signature title inclusive dates

Figure 7-2. Example of chain-of-custody record.

7.3 LABORATORY CUSTODY

The following protocol will be followed for all samples received at the Radian laboratories.

a. The laboratory has designated Jim McGaughey as sample custodian. The laboratory will set aside a sample storage security area. This will be a clean, dry, isolated room with sufficient refrigerator space that can be securely locked from the outside.

b. Samples will be handled by the minimum possible number of persons.

c. Incoming samples, along with the sample analysis request form (Figure 7-3), will be received only by the custodian, who will indicate receipt by signing the chain-of-custody record and sample analysis request sheets accompanying the samples, and retaining the sheets as a permanent record. Couriers picking up samples at the airport or post office shall sign jointly with the laboratory custodian.

d. Immediately upon receipt, the custodian places the samples in the sample room, which will be locked at all times except when samples are removed or replaced by the custodian. The samples are then cross checked with the enclosed chain-of-custody record to ensure that the proper number of samples were received and that they correspond to the appropriate sample descriptions. Samples are also checked for damage and/or leaks. All abnormalities will be documented.

e. The custodian will ensure that the samples are logged into the laboratory "master" sample log immediately upon receipt.

f. Only the custodian will distribute samples to personnel who are to perform tests.

g. The analyst will record in his laboratory notebook or analytical worksheet, identifying information describing the sample, the procedures performed, and the results of the testing. The notes will be dated, will indicate who performed the tests, and will include any abnormalities that occurred during the

SAMPLE ANALYSIS REQUEST

Part I: FIELD SECTION

Collector _____ Date Sampled _____ Time _____ hours

Affiliation of Sampler _____

Address _____
number street city state zip

Telephone (___) _____ Company Contact _____

Laboratory Sample Number	Collector's Sample No.	Type of Sample[a]	Field Information[b]

Analysis Requested _____

Special Handling and/or Storage _____

Part II: LABORATORY SECTION[b]

Received by _____ Title _____ Date _____

Analysis Required _____

[a]Indicate whether sample is water, soil, sludge, etc.

[b]Use back of page for additional information relative to sample location.

Figure 7-3. Sample analysis request.

testing procedure. The notes will be retained as a permanent record in the laboratory.

h. Laboratory personnel are responsible for the care and custody of a sample once it is handed to them and should be in their possession and view or secured in the laboratory at all times from the moment it was received from the custodian until the tests were run. Sample preparation forms will be drafted for each sample and include provisions for conducting and reporting:
   1. blank determinations for all reagents which become an integral part of the sample
   2. clean-up reagent blank determination
   3. glassware blank determination.

   All samples will be refrigerated prior to analysis to ensure adequate sample preservation.

i. The laboratory area shall be maintained as a secured area and shall be restricted to authorized personnel.

j. Once the sample analyses are completed, the unused portion of the sample, together with identifying labels and other documentation, must be returned to the custodian. The returned, tagged sample should be retained in the custody room until permission to destroy the sample is received by the custodian.

k. Samples should be destroyed only upon the order of the Program Manager when it is certain that the information is no longer required, or that the samples have deteriorated.

l. Figure 7-4 presents the complete chain-of-custody flow of samples from initial sampling to the reporting of results.

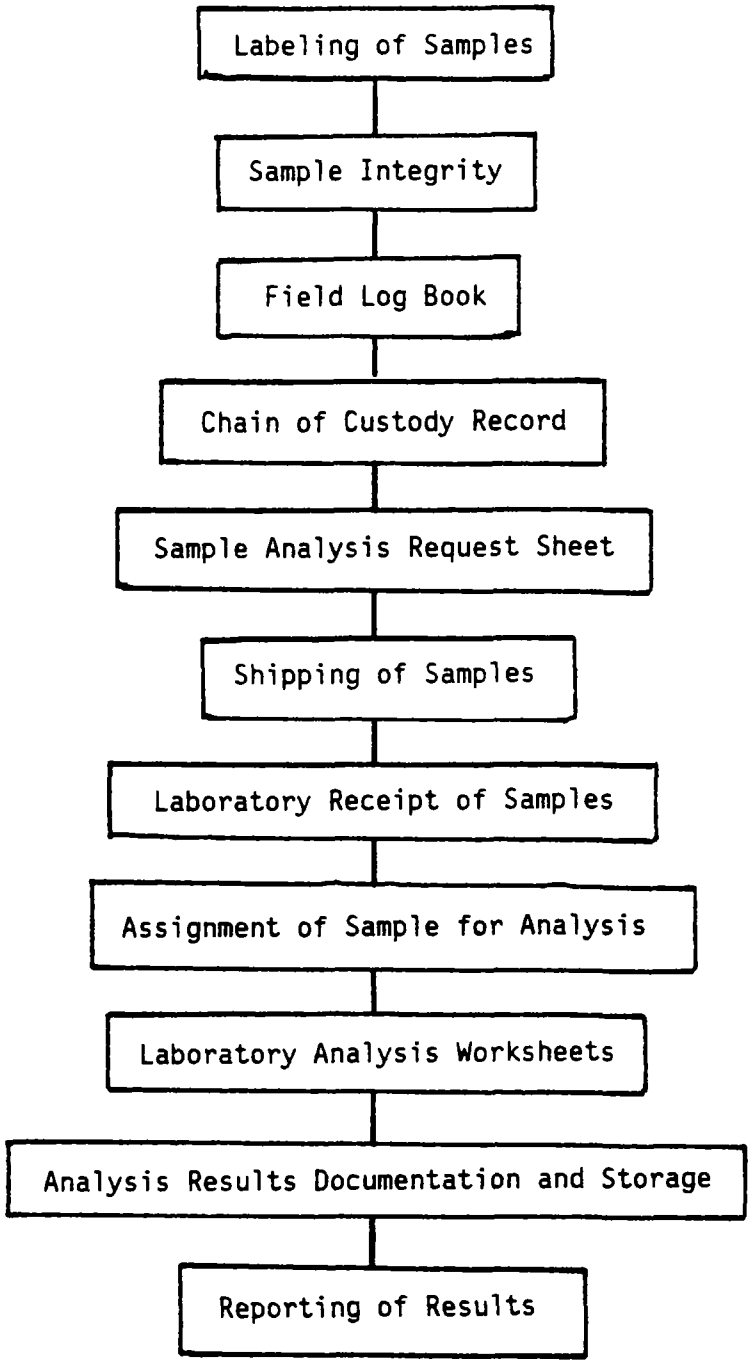


Figure 7-4. Chain of custody.

8. CALIBRATION PROCEDURES AND FREQUENCY

Calibration procedures for laboratory instrumentation will be performed on a daily basis to establish linearity of parameters being measured and determine response factors. This is the general approach that will be used throughout the project for each measured parameter. Analytical standard materials to be utilized will come from existing stocks or will be purchased from Ultra Scientific. Lot numbers will be documented for each standard along with date of receipt, date of initial use, expiration date, purity, and persons handling standards.

Complete traceability of each standard used for calibrations will continue by documenting all preparation steps from primary to working standards. A separate standard preparation quality control log book will be kept which will include weight measured, dilution volumes, calculations, solvents, solvent brands and lot numbers, and persons performing these procedures.

The calibration curve will be done at two concentrations for each calibration curve, one near the lower end of the curve and another at the high end of the curve. The individual readings of the calibration check points must both fall within the 95 percent confidence intervals of the original calibration curve.

The calibration curve is assumed to be linear. If the regression coefficient is less than 0.900, the calibration curve is not considered to be valid and the calibration is repeated with new standards.

Any failure of the analysis internal standard checks, or any failure of the calibration check causes the analyses to stop for that day until a new acceptable calibration curve is established.

8.1 CALIBRATION REQUIREMENTS FOR LABORATORY EQUIPMENT

Table 8-1 presents calibration requirements for laboratory equipment.

8.2 CALIBRATION STANDARDS

Specific chemical or physical species are available as standard reference materials or commercially available secondary standards. A list of these is provided in Table 3, page 29 of EPA-600/7-78-201, dated October 1978. In addition, certain "quality control" standards are available to check performance after calibrations for some tests. (See EPA QA Newsletter, dated February 1980, Volume 3, No. 1.) The use of these standards is to be specified in the procedure, and will include the frequency of calibration and limits of permissible deviation.

8.3 CALIBRATION RECORDS AND SUPPORT

Maintenance of calibration records will be required to provide assurance that required calibrations of measurement systems are occurring at specified intervals. A dated tag will be attached to the measurement system indicating expiration date of the calibration and type of standard. Tagged equipment will include:

- Balances
- Gas chromatographs
- Gas chromatograph/mass spectrometer system
- IR, UV, IC instruments.

Calibrations which are part of the measurement system preparation procedure (such as GC/MS, GC, IC, etc.) will be recorded in an instrument log book to be kept adjacent to the instrument. The log book will record the date, concentration versus response data, graphs, equations, preventive maintenance, parts replaced, etc.

8.4 CALIBRATIONS REQUIREMENTS FOR FIELD EQUIPMENT

The Method 5 dry gas meters in the control boxes will be calibrated before and after testing against a wet test meter standardized through the EPA Method 5 external national audit program.

All temperature measuring devices will be calibrated against an NBS thermometer.

Table 8-1. CALIBRATION REQUIREMENTS FOR LABORATORY EQUIPMENT

Item	Calibration method	Frequency of calibration	Calibration recommendation reference	Reference standard used
Analytical Balances	Standard weights	Monthly	(5)	NBS Class S weight
Microbalances	Standard weights	Each use	(5)	NBS Class J or Class N weights
Thermometers	Water bath check vs. standard	3 months	(6)	Certified NBS thermometer
Gas chromatography	Retention time/ detection response check	Each use-day	(4)	Reference mixture
	Response curve check	Each use-day	(6)	Reference mixtures
	Oven temperature check	Monthly	(4)	Reference pyrometer, thermocouple, or thermometer
GC/MS	MS tuning	Daily	(7)	DFTPP, BFD, or BFB
	Calibration check	Each 8 hours of analysis	(8)	See Table 3.1 of of Reference (8)

(4) EPA 600/4-78-043, August 1978, pp. 39-44.
(5) QA practices for Health Laboratories, S.L. Inhorn, APHA, (1978).
(6) TRW practice.
(7) EPA Method 624.
(8) "Development of Acceptance Criteria for the Determination of Organic Pollutant at Medium Concentrations in Soil, Sediment, and Water Samples, Systems, Science and Software #R-81-4819, April 1981. See also R-81-5042, June 1981 and #R-81-5043, June 1981.

9. ANALYTICAL PROCEDURES

The cyanide methods are contained in the Appendix to this report. In general, there are three methods of analysis described here. They are specific ion electrode, titrametric, and colorimetric. The colorimetric method with cyanide distillation apparatus appears to be the most accurate. It has the lowest minimum detectable limit and removes from the sample most interferences. Its only limitation is that it is a time consuming technique. For this reason it is proposed that a combination of analytical techniques be used. The specific ion electrode is a quick method and if the data generated can be confirmed by the colorimetric/distillation method the data could be acceptable.

A problem with analytical techniques for cyanide (liquid) is the short shelf life of the cyanide sample(<24 hours) which mandates analysis in the field rather than in the laboratory. With the specific ion electrode a sample degradation chart could be obtained for these samples in the field.

An alternative method to the three listed in the Appendix is the use of an ion chromatograph which could give accurate timely measurements to a much lower detection limit. Time would be required, however, to run a validation study to determine if this technique would be applicable for the gaseous and process samples obtained during this test.

9.1 METALS ANALYSIS

The screening and quantitation for metals will be analyzed by atomic absorption spectroscopy (AAS), and inductively coupled plasma emission spectroscopy (ICAP) techniques. Two modes of analysis will be ued for these species: direct analysis from solution, or cold vapor/ hydride evolution. The samples containing metals are prepared for analysis by acid digestion procedures. For all metals, except arsenic,

selenium and mercury, the solution resulting from the digestion procedures will be aspirated directly into the flame AAS, or into the plasma for ICAP. For selenium and arsenic, the solution is treated to form the hydride and then is detected by the AAS method. For mercury, the solution resulting from the digestion of the samples is reduced with stannous sulfate which reduces the ionic mercury in the sample to the atomic species. The volatile mercury is swept from the sample in a closed system through an absorption cell. The level of mercury in the sample is obtained from the integrated AAS signal formed during its evolution from the sample.

10. DATA ANALYSIS, VALIDATION AND REPORTING

The data reduction procedures to be used in calculating the concentration or value of all measured parameters in this program are required as part of the procedural write-up. However, it must be recognized that the final information to be derived from such data is dependent upon a complex sequence of data flows, beginning at the site sampling/measurement activity and terminating only after a final review of all data from various laboratories (including subcontracting laboratories) has been completed. The quality of the final information cannot usually be altered by repeat testing in the final stages of data review. An ultimate removal of outlying data, while improving the accuracy and validity of the data base, reduces the data completeness, sometimes below acceptable limits. It is therefore highly important that early data reviews be made in the data scheme so that timely corrective measures can be taken.

The approach taken in this program to maintain quality consists of implementing timely data reviews at the data generation source whenever possible.

10.1 FIELD DATA QUALITY REVIEWS

	Objective	Action	Responsible Person
1.	Sample and process information conforms to conditions and schedule in Section 6	Review of labeled samples and in-process samples using daily sample inventory	Sample Custodian
2.	Verify incoming data and sample completeness	Daily count of incomplete items	Sample Custodian

	Objective	Action	Responsible Person
3.	Verify completeness of field notebooks	Review Daily	Test Systems Site Manager
		Calibration criteria reviewed and test calibration acceptance recorded	Site Chemist
4.	All data forms are completely filled out	Review and check off during each test. Forms provided by supervisor with non-required entries marked	Site Chemist

10.2 LABORATORY DATA QUALITY REVIEWS

	Objective	Action	Responsible Person
1.	Verify incoming data and sample completeness	Daily count of number and nature of samples received versus number and nature of entries made in log. Mark verified on log	Sample Custodian
2.	Verify all data forms completed	Review and check off during each test. Forms provided by supervisor with non-required entries marked out.	Technician
3.	Manual data reduction procedures	Daily review sample rank of calculated values against sample rank of raw data values. Rank to be the same.	Technician
4.	Computer data reduction procedures	After daily set up, verify retrievability of data in memory. Check off in calibration log.	Technician
5.	Verify completeness of field notebooks	Review Weekly	Laboratory Manager
		Calibration criteria in method reviewed and test calibration acceptance recorded.	Laboratory Chemist
		Record values of replicate analyses	Laboratory Chemist

10.3 ENGINEERING DATA QUALITY REVIEWS

	Objective	Action	Responsible Person
1.	Assure completeness of field and lab data.	Compare field and lab data forms against data list at each use and check off	Project Manager
2.	Assure comparability of units	Review units reported for consistency in calculations at each use and check off.	Project Manager
3.	Examine engineering validity of data	Review process parameter extremes and transients versus data gathering times. Document any data excluded on this basis.	Project Manager
4.	Examination of statistical data homogeniety	Apply outlier tests to data groupings to be used. Record data and test results.	Project Manager

This review is also accomplished on a spot check basis by the Field Sampling Leader and the Project Manager. This review refers to the final data assessment step.

10.4 DATA BASE OUTLIER REVIEW

Three kinds of outlier reviews will be made during the engineer review in this program:

1. Values reported by data gatherer as associated with an atypical circumstance. Engineering judgement of the effect of the recorded anomaly on the datum will be made. The datum will be rejected if the magnitude and direction of the anomaly, compared to known effects, is sufficient to exceed the factor of 2 reproducibility, $CV_2 = .63$ (Section 14).
2. Values identified by data reviewer as nonrepresentative of the generalized circumstance being assessed. Process data reviews will be used to establish a nonrepresentative condition if present. One kind of nonrepresentative data would be data obtained during a controlled condition test phase in which the controlled condition did not comply with the specifications called for in the test plan.

Data obtained during non-normal test conditions may be acceptable and representative so long as the test and process conditions are known.

Representativeness expresses the degree to which data accurately and precisely typifies a characteristic of a population, parameter variations at a sampling point, a process condition, or environmental condition.

3. Values identified by inspection of results to be possible statistical outliers. The Dixon outlier test (see Section 14) will be applied to suspect data points at the 5 percent significance level. Data strongly suggestive of belonging to a logarithmic normal distribution rather than a normal distribution will be transformed to their logarithm before applying the test. A log normal distribution is suggested when the standard deviation(s) of the measurements varies with the mean value, ($\bar{x}$), such that the coefficient of variation, $s/\bar{x}$, is constant. In this instance, two groups of data may be suspected, rather than an outlier to a single group. All outlier usage will be reported with the final data.

10.5 QUALITY MEASUREMENT

The quality of data analysis, validation, and reporting in this program will be maintained by early personnel indoctrination, review of technical understanding by the QA office, the provision for data forms to be encountered at various steps of the data gathering processes as part of the test plan, and by the examinations provided in Sections 10.1, 10.2, and 10.3 done by data processors at various levels. Experience has shown that many of the errors introduced into the data during recording and data reduction procedures are detected by subsequent checking; however, in some instances correction is made impossible by time lapses or sheer quantity of raw data sheets which would have to be searched. The major quality effect in such instances is then a decrease in completeness of the data.

The completeness check indicated for the field and laboratory custodian and for the engineering data processors in Sections 10.1, 10.2, and 10.3 will provide interim check points for preventing such

completeness lapses. The check is performed and recorded by the person receiving the transfer of information from a previous step.

10.6 LABORATORY DATA SYSTEM

This wide range of analytical activity in this project will produce a large and equally diverse amount of data. TRW has acquired a laboratory data system capable of storing, analyzing, and graphically presenting data of this nature. The data system consists of three components; (1) a Varian Vista-401 dedicated chromatography data system, (2) a microprocessor based computer system, and (3) a Hewlett-Packard 5985A Gas Chromatography/Mass Spectrometry/Computer System (see Figure 10-1).

The Vista-401 Data System, as configured in TRW's Eastern Operations laboratory, consists of a 68K microprocessor based data acquisition system capable of simultaneously monitoring four chromatographic channels, two dual channel printer/plotter units, and 200K of on-line floppy diskette storage. Analysis methods can be programmed into this system, stored in main memory or on diskette, and be used to monitor any of the four data channels. The Vista-401 is capable of plotting, on the fly, chromatograms from any or all of the data channels, and archiving this data in its complete form on diskette storage for later analysis. Post-run calculations, including peak area integration and retention time assignment, can be performed on data stored either in main memory or on diskette. All information concerning sample identification, analysis conditions, and results of post-run calculations is automatically documented upon completion of each analysis. The laboratory microcomputer is connected to the data acquisition system through a standard RS-232 serial interface which enables the transfer of raw chromatographic data and processed post-run reports from the Vista-401 to the microcomputer.

The laboratory microcomputer system consists of a 64K eight bit Apple microprocessor, 340K of online floppy diskette storage, a high speed printer, and a digital X-Y Plotter. This general purpose computer system greatly extends the range of data analysis capabilities available to the analyst. Computer programs have been written for linear regression analysis, statistical calculations, sample log-in and analysis

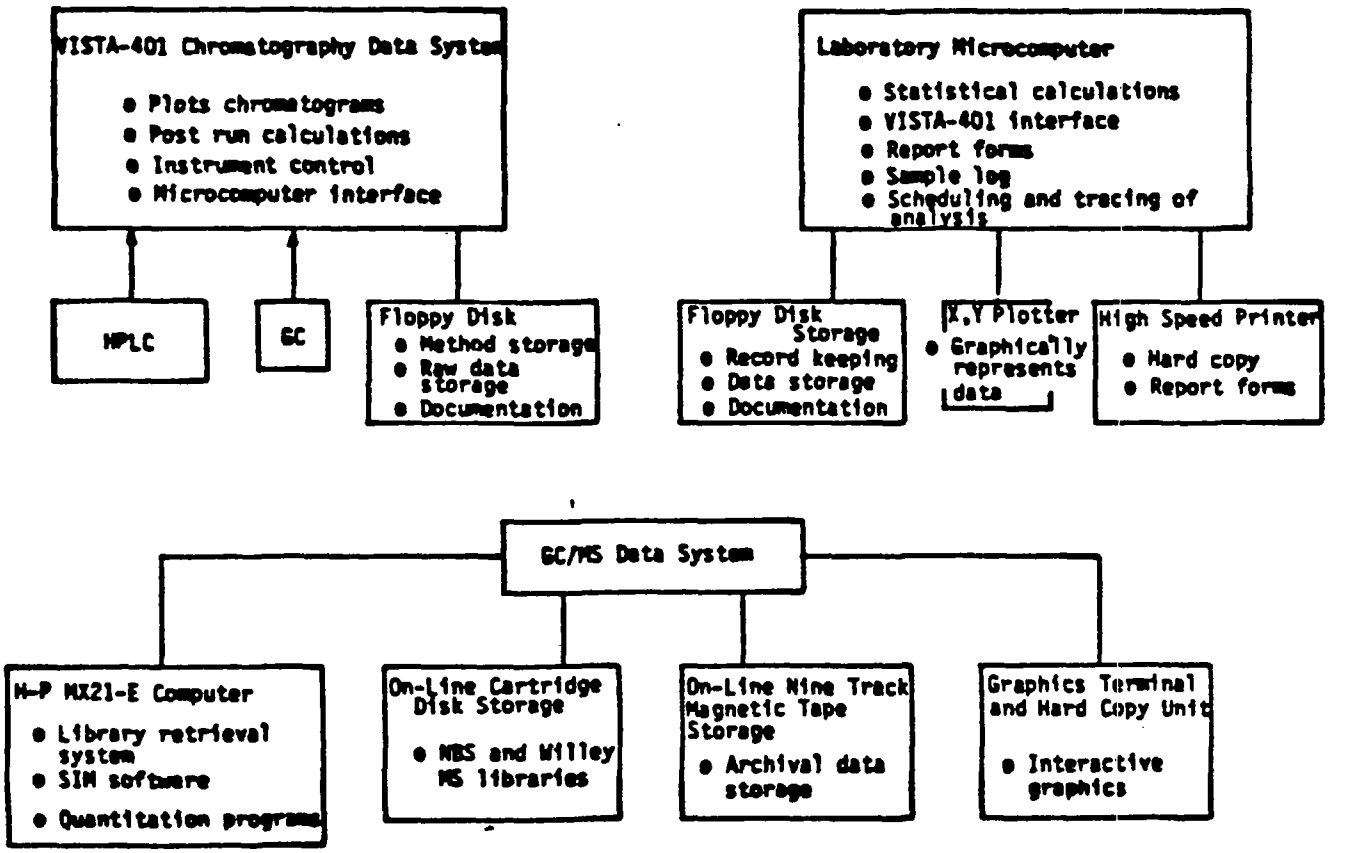
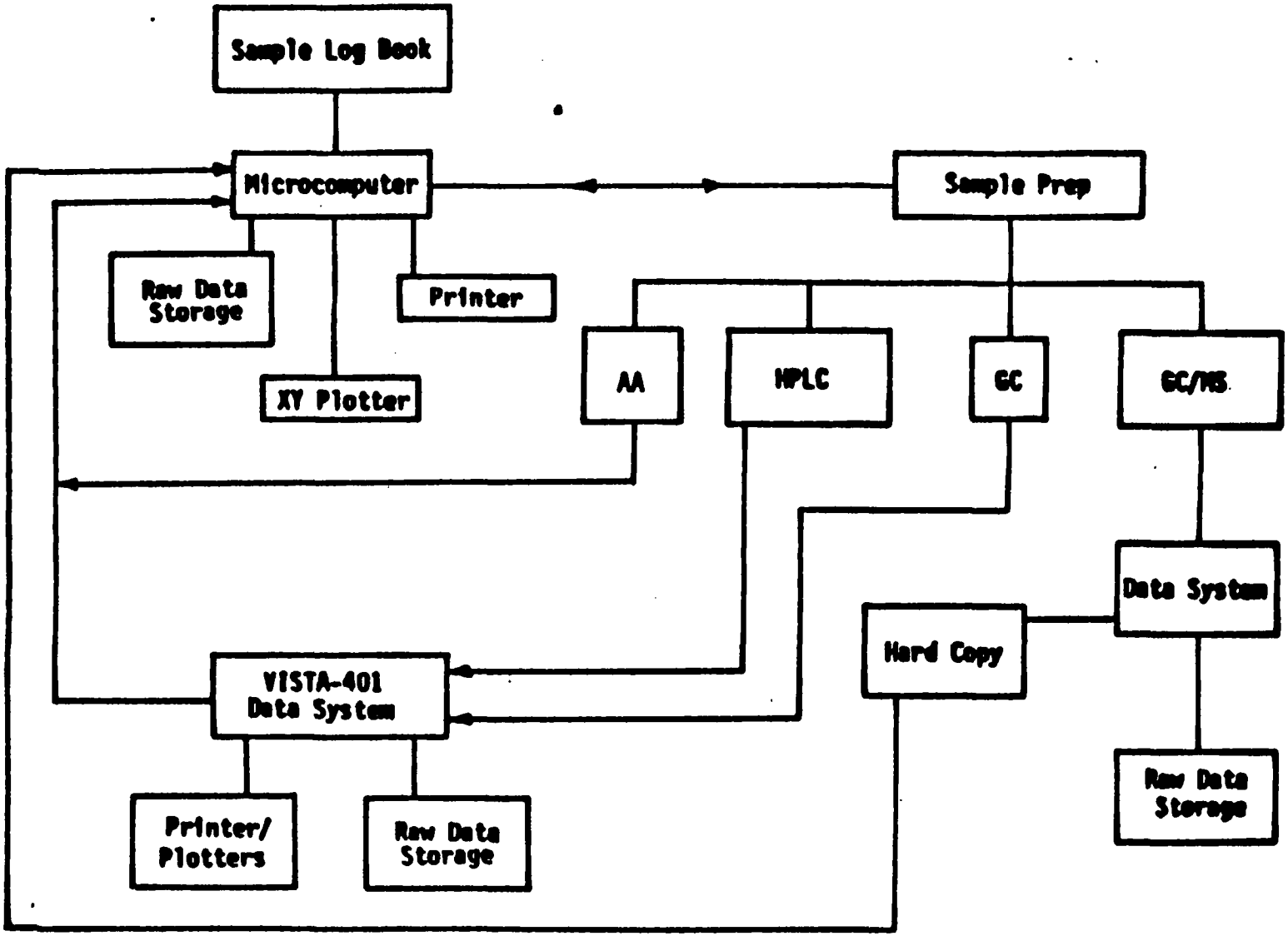


Figure 10-1. Data reduction and validation.

tracking, data report generation, and graphical presentation of QC charts, calibration curves, and project resource allocation charts.

The GC/MS/Computer system consists of a 32K, sixteen bit minicomputer, 20 megabyte of online cartridge disk storage, nine track magnetic tape storage, and a graphics terminal. Computer software is provided for the collection, storage, graphical presentation, and identification of data from either direct probe/MS or GC/MS analysis. Both the NBS and Wiley Mass Spectral Libraries are stored on cartridge disk for library retrieval search identification. The GC/MS data system allows data collection in either a selective ion monitoring or full scanning mode. All data collected is stored on-the-fly onto the cartridge disk, and can be transferred to magnetic tape for archival storage upon completion of the analysis.

The utilization of the laboratory data system is diagrammed in Figure 10-2. After a sample is entered in the laboratory sample log, the microcomputer assigns it a diskette master record file. The microcomputer then creates an analysis schedule for the sample, storing the projected completion dates of each assignment in the sample record file. Analysis assignment forms are then generated using the high speed printer, and the sample is routed to the appropriate instrument. Upon completion of each analysis, the status of the schedule of analyses is updated, new analysis assignment forms are printed out, and the sample is sent to the next instrument. Data from HPLC and GC analyses are acquired by the Vista-401 system, plotted, stored on floppy diskette, and transmitted to the microcomputer. Mass spectrographic data are collected by the GC/MS data system, stored in real time on cartridge disk, archived on magnetic tape, and encoded by the analyst into the microcomputer. Data from the atomic absorption spectrophotometer are manually fed into the microcomputer. The physical storage location of all data (including that on magnetic tape, cartridge disk, floppy diskette, and all chromatograms and X-Y Plotter graphs) is entered into the master record file for each sample. In this manner, the exact status of each analysis for any sample and the storage location of all of its data will be instantly available by querying the memory through the microcomputer console.



1) Sample logged into Master log book and computer according to analyses.
2) Computer tracks types of analyses performed and status.
3) HPLC and GC analyses in VISTA-401
4) VISTA-401 interfaces with computer.
5) GC/MS results transferred to microcomputer.
6) XY plotter graphically presents data.

Figure 10-2. Data flow and sample scheduling.

Once the data have been input to the microcomputer, the appropriate computer programs are implemented for the reduction of the data to the final report format. These results are then output on the high speed printer or X-Y Plotter.

10.7 DATA ANALYSIS AND VALIDATION

The reliability and acceptability of environmental analytical information depends upon the rigorous completion of all the requirements outlined in the QA/QC protocol. The elimination of any one step without a valid reason could easily jeopardize the entire testing program. Data analysis and validation is the process whereby data are filtered and accepted or rejected based on a set of criteria. This involves a critical review of a body of data in order to locate and isolate spurious values. It may involve only a cursory scan to detect extreme values or a detailed evaluation requiring the use of a computer. In either case, when a spurious value is located it is not immediately rejected. Each questionable value must be checked for validity. A comprehensive record of all questionable data, whether rejected or not, will be maintained along with rejection criteria and any possible explanation for their being questioned. A detailed approach such as this can be time consuming, but can also be helpful in identifying sources of error, and in the long run, save time by reducing the number of outliers.

Prior to any statistical approach, the reported data will be checked to ensure that it was accurately transcribed. Often times hard copies of raw data are not available directly from a measuring device. Here, the values must be accurately and legibily recorded. A quick double check of the value and a comparison to previously recorded data will be performed. Additionally, the use of prepared data recording forms conveniently formatted and bound is essential. Hard copies of data can also be obtained directly from measuring devices which are equipped with the necessary digital recording peripheral. Usually, this method of recording data is sufficient if the hard copies are properly labeled and filed. However, periodic checks will be performed to ensure the proper operation of such a device.

The collected data will be reviewed at a minimum by the analyst, his superior, and the QC coordinator. The data will be scrutinized at

least daily to eliminate the collection of invalid data should the measuring devices not be operating properly. The analyst will not hesitate to record any unusual instances (no matter how minor) in the daily cycles (such as power loss or fluctuations, temporary leaks or adjustments, or operator error).

Once the data have been confidently recorded and logically formatted, at least two working copies will be made. The original shall be stored by the program manager. The data can now be statistically validated either manually or by computer. In either case, the criteria applied to the data will depend on the individual measurement processes and the ultimate purpose of measurement. Confidence in the accuracy of analytical results and improvements in analytical precision is established by identification of the determinate sources of error. Precision is governed by the indeterminate error inherent in the procedures, and can be estimated by statistical techniques. To ensure the accuracy of a result, the quality control procedure must be without bias. Techniques have been developed for the elimination of bias.

Statistical data analysis control involves application of the laws of probability. This technique is employed to detect and separate assignable (determinate) from random (indeterminate) causes of variation. "Statistics" is the science of uncertainty. Any conclusions based on statistical inference contain varying degrees of uncertainty, which are expressed in terms of probability. Uncertainty can be qualified in terms of well defined statistical probability distributions. These probability distributions can be applied direct to quality control. The application of statistical quality control can most efficiently indicate when a given procedure is in control. A continuing program that covers sampling, instrumentation, and overall analytical quality will assure the validity of the analytical program.

All analytical methods are subject to experimental errors. Determinate errors contribute constant error or bias whereas indeterminate ones produce random fluctuations in the data. The concepts of accuracy and precision as applied to the detection and control of error have been clearly defined and will be used exactly.

The terms "determinate" error, "assignable" error, and "systematic" error are synonymous. A determinate error contributes constant error or bias to results which may agree precisely among themselves. A method may be capable of reproducing results to a high degree of precision, but only a fraction of the component sought is recovered. A precise analysis may be inaccurate due to:

a. inadequate standardization
b. inaccurate volumetric measurements
c. inaccurate balance weights
d. improperly calibrated instruments
e. personal bias (color estimation)
f. consistent carelessness
g. lack of knowledge
h. calculation errors
i. use of contaminated or improper reagents
j. nonrepresentative sampling
k. poorly calibrated standards of instruments.

Determinate errors may be additive (the error has a constant value regardless of the amount of the constituent sought in the sample) or proportional (the error changes magnitude according to the amount of constituent present in the sample). Generally, determinate errors have a direct identifiable source and can be detected by such procedures as the use of "spiked" samples, control charts, or differing sample sizes.

Even though all determinate errors are removed from a sampling or analytical procedure, replicate analyses will not produce identical results. This erratic variation arises from random error indeterminate error, and may have several sources, e.g.:

a. variation in reagent addition
b. instrument response
c. line voltage transients
d. physical measurement of volume and mass.

In environmental analysis the sample itself is subject to a great variety of variability. Although indeterminate errors appear to be random in nature, they do conform to the laws of chance; therefore statistical measurements of precision can be employed to quantitate their effects.

A measure of the degree of agreement (precision) among results can be ascertained by analyzing a given sample repeatedly under conditions controlled as closely as conditions permit. The range of these replicate results (difference between highest and lowest value) provides a measure of the indeterminate variations.

Indeterminate errors can be estimated by calculation of the standard deviation (σ) after determinate errors have been removed. When indeterminate or experimental errors occur in a random fashion, the observed results (x) will be distributed at random around the average or arithmetic mean ($\bar{x}$).

Another useful and necessary technique to aid in data validation is the analyses of duplicate samples. Duplicate analyses are employed for the determination and control of precision within the laboratory and between laboratories. The control chart technique is directly applicable, and appropriate control limits can be established by arbitrarily subgrouping the accumulated results or by using appropriate estimates of precision from an evaluation of the procedures.

The QA functions in the project for data assessment are shown in Figure 10-3 and consist of the following:

- Verification of the acceptability of the computation steps and calculation checks used in the analytical procedures, including any computer programs for processing raw data
- Statistical evaluaton of comparisons between standards, replicates, spiked samples, and the routine analyses
- Records and trend analyses to identify potential QA problem areas in the assessment scheme
- Definition of data validation procedures for all measurement systems
- Provision for clear definition of various parameters, such as flow rates and calibration data
- Use of minimum detectable limits to evaluate trace data for appropriateness
- Examination of outliers immediately for possible cause, error, or interferences

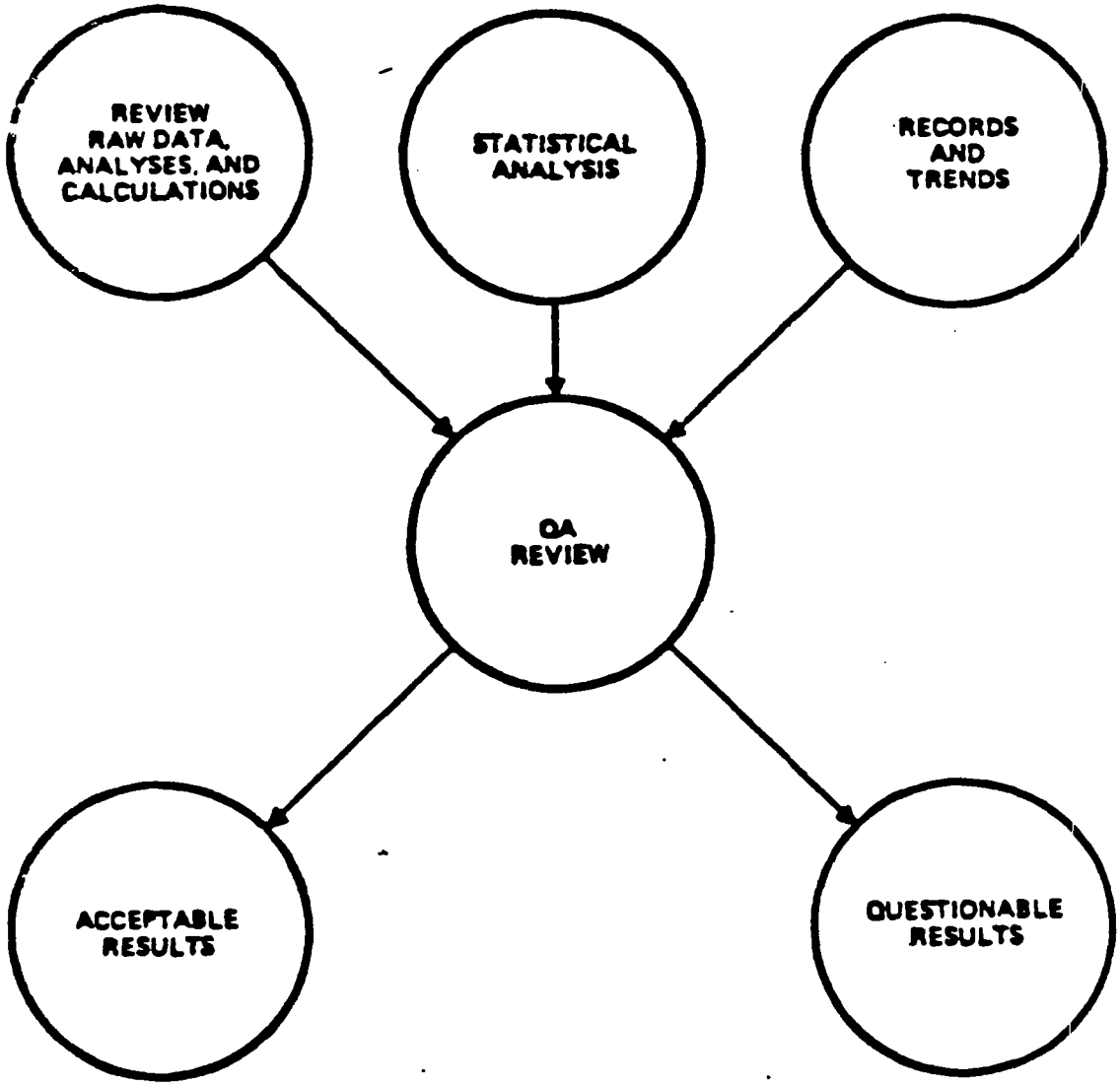


Figure 10-3. Activities for data quality validation and assessment.

- Concern with all rejected data and the cause or reason for rejection
- Relation between data and standard, replicates, and spikes
- Definition of a reporting scheme.

An important aspect of QA is the establishment of a mechanism for problem detection, reporting, and correction. It is vital that the problems encountered and corrective actions taken be thoroughly documented. Quality summary reports will be prepared and distributed to the project manager and appropriate levels of management. This report will address the following:

- Assessment of measurement data accuracy
- Results of system audits
- Significant quality problems and recommended solutions
- Names of persons responsible for corrective action
- Major milestones involving data quality.

In addition, these reports will serve as a basis for data quality reports to be supplied to the EPA.

The equations used to calculate values of measured parameters are available at the TRW laboratory. Data reduction programs for the gas chromatographs are stored in one of the computers and follows a standard peak area integration program.

Both the GC/MS and the GC/FID are Hewlett-Packard instruments and have their automatic internal integration devices which are generally accepted techniques. These methods along with calibrations and a routine daily tune up are used to validate the results from these instruments.

11. INTERNAL QUALITY CONTROL CHECKS

Leak checks will be the primary internal quality control on the sampling systems. Prior to and after each test, the leak check must be less than 0.02 cfm or 4% of the total sample volume, whichever is less.

Internal quality control checks in the laboratory analysis procedures consist of daily calibration checks and monitoring an internal standard on each calibration check and on each sample. A multipoint calibration curve and response factors for NaCN will be developed. In order for the calibration to be valid, the regression coefficient must be greater than 0.90. The 95 percent confidence interval on an individual predicted y_0 (the response) for a given x_0 (the known concentration of the calibration standard) will be derived from the calibration data. Two calibration checks will be made daily covering the upper and lower ranges of concentration. The responses of these calibration checks must fall within the 95 percent confidence interval developed from the calibration data, or a new set of calibration standards must be made up, and a new calibration curve (and 95 percent confidence interval) derived.

12. PERFORMANCE AND SYSTEM AUDITS

The Program Manager and the Quality Assurance Officer for Radian will conduct performance and system audits on the records kept in the field and in the laboratory.

Radian will analyze external audit samples as appropriate if requested and approved by the EPA Project Officer.

13. PREVENTIVE MAINTENANCE

Radian's preventive maintenance program involves periodic assessment of all instrumentation and equipment being used. Instrument log books are kept by noting major repairs, modifications, and the next service date.

The following table provides a minimum schedule of maintenance.

Item	Maintenance	Frequency	Documentation
GC/FID	Full servicing	Quarterly, and as needed	Instrument log, tag
GC/TC	Full servicing	Quarterly, and as needed	Instrument log, tag
GC/ECD	Full servicing	Quarterly, and as needed	Instrument log, tag
GC/MS	Contract	Quarterly, and as needed	Instrument log
Field Meter Box	Full servicing	As needed	Calibration log

At the present time there are no spare parts that can be classified as critical or in short supply. Gas chromatographs require little preventive maintenance, but close attention to standards and quality control charts must be done to alert the analyst of problems. Instrument manuals and trained troubleshooters are on hand to resolve quickly any problems encountered. Capillary systems are evaluated initially and then periodically by injecting a standard test mixture to determine column efficiency, leaks, detector response, and injector function.

Gas chromatography/mass spectrometry systems at Radian are periodically maintained through a maintenance contract with the manufacturer

who performs a quarterly preventive maintenance call and checkout of the complete system and who is on-call within 48 hours as necessary. A log book is kept on all service calls, and also on the types of samples analyzed.

During field sampling a complete set of spare sampling equipment, glassware, and supplies will be available. Spare O_2 and CO/CO_2 monitors will be available. A complete Orsat® apparatus will serve as a spare for the GC/TC apparatus.

13.1 QUALITY MEASURES

Preventive maintenance will be reviewed by means of a weekly equipment downtime report to be provided to the quality office by the supervisor of each field or laboratory station. This report is required only in the event of equipment or test downtime. The report will include:

- the instrument identity,
- the nature of the problem,
- the required action,
- the percent downtime, and
- the reason for downtime.

The instrument is to be assumed available over the hours regularly scheduled for its usage, the downtime is to be considered the actual hours lost by the failure.

The report is only required in the event of inability to conduct the test because of lack of hardware, supplies or chemicals.

14. PROCEDURES USED TO ACCESS DATA PRECISION, ACCURACY, AND COMPLETENESS

The precision and accuracy of data must be routinely assessed on all environmental monitoring and measurement data. The specific procedures necessary to assess the quality of the data on a routine basis are discussed in the following paragraphs. Such routine statistical procedures applied to a great bulk and variety of samples can become quite cumbersome. To avoid this, an inhouse computer will be utilized to expedite the performance of statistical calculations. Standardized statistical program packages will be used to calculate any necessary parameters quickly and accurately, store and/or list previous values, and plot the data in the form of control charts.

The statistical techniques which best suit the needs of a given test procedure will be chosen to ensure the routine assessment of data precision, accuracy, and completeness. The following is a summary of examples of statistical techniques used in handling environmental measurement data which is in turn followed by an individual listing of each in more detail.

- Central tendency and dispersion
  - Arithmetic mean
  - Range
  - Standard deviation
  - Relative standard deviation
  - Geometric mean
- Measures of variability
  - Accuracy
  - Bias
  - Precision; within laboratory, between laboratories, and laboratory bias

- Significance test
  - u-test
  - t-test
  - F-test
  - Chi-square test
- Confidence limits
- Testing for outliers
- Control charts

14.1 CENTRAL TENDENCY AND DISPERSION

A. The Arithmetic Mean

The sum of all values in a measurement set (X_i), divided by the number of values summed (n), is the definition of the arithmetic mean, commonly called the "average." It is often denoted symbolically by a bar over the variable symbol, as "$\bar{X}$".

$$\bar{X} = \sum_{i=1}^{n} X_i/n$$

B. Range

The difference between the maximum and minimum values of a set of values defines the range.

$$R = X_{max} - X_{min}$$

A rough indication of variability, particularly when the set of values is small (<10).

C. Standard Deviation

A standard deviation is an indication of the dispersion of a set of numbers about the mean value. Normal (and other) distributions are expressed as a function of the standard deviation.

For a given set of values, an equation to calculate s is:

$$s = \frac{\left(\sum_{i-1}^{n} X_i^2 - \left(\frac{\sum_{i=1}^{n} X_i}{n}\right)^2\right)^{\frac{1}{2}}}{n-1}$$

D. Relative Standard Deviation (RSD), or Coefficient of Variation (CV)

The dispersion of a set of values is expressed as a percentage of the mean.

$$\%RSD = (s/\bar{X}) \times 100$$

14.2 MEASURES OF VARIABILITY

A. Accuracy

Accuracy is defined in terms of the bias, B, which is the difference (either on an absolute or percentage basis) between a measured value and an assumed "true" value. The larger the difference, the lower the accuracy.

$$B = X - T, \text{ or}$$

$$\%B = \frac{X-T}{T} \cdot 100$$

B. Recovery

For spiked samples the recovery (REC) can be defined as a measure of accuracy as follows:

let c_o = measured concentration analyzed in the sample without the addition of a spike, mg/kg

c^1 = concentration of a standard solution mg/L

v_{s_1} = volume of standard added to the sample for Spike No. 1, mL

c_1 = measured concentration analyzed in the sample after adding Spike No. 1, mg/kg

$$REC = \frac{c_1 - c_o}{(c^1 \times v_{s_1} \times 10^{-3})}$$

or on a percentage basis

$$\% \text{ REC} = \frac{c_1 - c_o}{(c^1 \times v_{s_1} \times 10^{-3})} \times 100$$

Note that % Recovery would be related to % B, percent bias, as follows:

$$\% \text{ B} = 100 - \% \text{ REC}$$

C. Bias

Bias is a nonrandom measurement error: a consistent difference either between sets of results or between a measured value and a "true" value.

D. Precision

A measure of agreement among individual measurements of a variable, under identical or specified similar conditions. Precision may be expressed in several ways, and care must be exercised in the definition and use of precision measures.

One set of such measures* follows:

1. Within-laboratory: The within-laboratory standard deviation, s, measures the dispersion in replicate single determinations made by one laboratory team (same field operators, laboratory analyst, and equipment) sampling the same true concentration. This is also termed the repeatability.

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*These definitions are taken from EPA collaborative test result publications, and are applied to the various federal reference sampling and analysis techniques.

2. Between-laboratory: The between-laboratory standard deviation, s_b, measures the total variability in a determination due to determinations by different laboratories sampling the same true concentration. The between-laboratory variance, s_b^2, may be expressed as:

$$s_b^2 = s_L^2 + s^2$$

and consists of a within-laboratory variance plus a laboratory bias variance, s_L^2 (usually termed reproducibility).

Laboratory bias: The laboratory bias standard deviation,

$$s_L^2 = s_b^2 - s^2$$

is that portion of the total variability that can be attributed to differences in the field operators, analysts and instrumentation, and due to different manners of performance of procedural details left unspecified in a technique. This term measures that part of the total variability in a determination which results from the use of a technique by different laboratories, as well as from modifications in usage by a single laboratory over a period of time. The laboratory bias standard deviation is estimated from the within- and between-laboratory estimates previously obtained.

A corresponding set of relative standard deviations would be RSD, RSD_b, RSD_L. These are convenient to use if the precision is proportional to the mean value of the variable.

14.3 SIGNIFICANT TESTS

A. u-Test

This test measures the significance of individual values and experimentally estimated means where the normal population has a known mean and standard deviation.

$$u = \frac{X - \bar{X}}{s}$$

where

X = individual value being tested

$\bar{X}$ = calculated mean of experimental results

s = calculated standard deviation of all data in population

u is a measure of the number of standard deviation units an individual data point is away from the mean, assuming normal distribution.

B. t-Test

If one has an assumed "true value," μ_o, however obtained, the existence of a significant bias in other measurements of this value can be defined by as t-test:

$$t = \frac{\bar{d}}{s_d/\sqrt{n}}$$

where $\bar{d} = (\bar{x} - \mu_o)$

where

t = a parameter, the magnitude of which is referenced to tabulated values. A t-value which exceeds the tabulated value for given specifications of probability and number of degrees of freedom indicates the existence (within the definition of probability specified) of a significant bias. The more stringent the probability requirement; i.e., the smaller the probability chosen, the larger the tabulated t-value.

d = the average of the signed difference between the true value and the measured values; the average bias.

s_d = the standard deviation of the signed differences, d_i.

n = the number of measurements made.

C. F Test

Fisher's F statistic is used in testing whether two sets of samples could have come from normally distributed populations having the same variance, σ^2. The assumption involved in the test is that the samples are random and independent of one another and are selected from normally distributed populations. The first set has n_1 samples, and the second set has n_2. The degrees of freedom are $v_1 = n_1 - 1$ and $v_2 = n_2 - 1$ for the two sets of samples. The statistic, F, is defined as

$$F \equiv \frac{s_1^2}{s_2^2}$$

and is distributed as Fisher's F with v_1 and v_2 degrees of freedom. If $F > F_{v_1, v_2, 1-\gamma/2}$ (with $s_1^2/s_2^2 > 1$), then the probability is $(1-\gamma)$ that the two sets of samples did not come from normally distributed populations having equal variances.

D. Chi-square test

If one has a reasonable estimate of the expected standard deviation of a set of measurements, the existence of a defined "excess variability" can be tested as follows:

$$\frac{\chi^2}{\phi} = \frac{s_d^2}{\sigma^2(x)}$$

where

χ^2/ϕ = a random variable with tabulated values ($\phi = n - 1$ = number of degrees of freedom).

$\sigma^2(x)$ = the expected variance of the measurements of x.

If χ^2/ϕ is larger than the chosen tabulated value (with specified probability), it is concluded that the measurements are exhibiting excess variability. The chi-square test is a measure of the validity of a series of measurements based on an "expected" variability. The test is worthwhile only whenever a measurement technique has been tested thoroughly, so that a realistic expectation can be estimated.

14.4 CONFIDENCE LIMITS OR INTERVALS

Confidence limits take two forms. One form for a mean or average value defines a numerical range within which one has a (arbitrarily chosen) probability of finding the true mean value of the measured variable. If the measurement variability is expressed as a standard deviation, the confidence limits as defined above can be calculated as follows:

$$CL = X \pm ts/\sqrt{n}$$

where all symbols have been previously defined. Note that as the number of measurements, n, increase, the magnitude of CL decreases. Also, for higher probabilities of containing the true mean within CL, the larger the value of t and therefore the larger the size of CL.

The second form of confidence limit defines an interval within which the next individual measurement can be expected to fall with a given probability. The calculation of this limit, sometimes called a probability limit on a specified type of tolerance limit, is by the following relationship:

$$TL = X \pm ts$$

While n, the number of measurements, does not explicity appear in the equation for TL, it does determine (along with the selected probability) the value of t; i.e., as n increases, t decreases.

14.4.1 Confidence Interval in Calibration Data (Linear Regression)

Calibration data most often consist of multiple values of the instrument response y_i for known values of concentration x_i. An equation $y = a + bx$ is sought so as to minimize the sum of squares of $(y_i - \hat{y}_i)$, where y_i are the experimental values of the response and $\hat{y}_i$ are the calculated values of the response, i.e., $\hat{y}_i = a + bx_i$. This is the method of least squares and results in the calculation of a and b for a set of x_i, y_i data (where $i = 1,\ldots,n$, the number of calibration data). The calibration curve is then

$$y = a + bx \qquad (1)$$

The calibration data for n = 5 are

x_i	y_i
x_1	y_1
x_2	y_2
x_3	y_3
x_4	y_4
x_5	y_5

The method of least squares gives

$$a = \sum_{i=1}^{n} (y_i)/n - b \sum_{i=1}^{n} x_i/n \tag{2}$$

$$b = \frac{n \sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n \sum_{i=1}^{n} x_i^2 - (\sum_{i=1}^{n} x_i)^2} \tag{3}$$

Other useful statistics are:

The residual mean square, s^2

$$s^2 = (\sum_{i=1}^{n} y_i^2 - a \sum_{i=1}^{n} y_i - b \sum_{i=1}^{n} x_i y_i)/(n-2) \tag{4}$$

The correlation coefficient

$$r = \frac{\sum_{i=1}^{n} (x_i-\bar{x})(y_i-\bar{y})}{\left[\sum_{i=1}^{n} (x_i-\bar{x})^2 \sum_{i=1}^{n} (y_i-\bar{y})^2 \right]^{\frac{1}{2}}} \tag{5}$$

$$r = \frac{n \sum_{i=1}^{n} x_i y_i - (\sum_{i=1}^{n} x_i)(\sum_{i=1}^{n} y_i)}{\left[\left(n \sum_{i=1}^{n} x_i - (\sum_{i=1}^{n} x_i)^2 \right) \left(n \sum_{i=1}^{n} y_i^2 - (\sum_{i=1}^{n} y_i)^2 \right) \right]^{\frac{1}{2}}} \tag{6}$$

The confidence interval on an individual predicted y_o, given x_o is

$$a + bx_o - t_{n-2,\ 1-\gamma/2}\left[1 + 1/n + \frac{(x_o-\bar{x})^2}{\sum_{i=1}^{n}(x_i-\bar{x})^2}\right]^{1/2} s < y_o < a + bx_o + t_{n-2,\ 1-\gamma/2}\left[1 + 1/n + \frac{(x_o-\bar{x})^2}{\sum_{i=1}^{n}(x_i-\bar{x})^2}\right]^{1/2} s$$

$t_{n-2,\ 1-\gamma/2}$ is the cumulative Student's t statistic having n-2 degrees of freedom and $(1-\gamma/2)$ level of significance. A 100 $(1-\gamma)$ percent confidence interval gives the following values for $t_{n-2,\ \gamma/2}$. Note that for the 95% confidence interval, $(1-\gamma/2) = 0.975$, and

n	$t_{n-2,\ 0.975}$
10	2.306
9	2.365
8	2.447
7	2.571
6	2.776
5	3.182
4	4.303
3	12.706

14.5 TESTING FOR OUTLIERS

An outlier is an extreme value, either high or low, which has questionable validity as a member of the measurement set with which it is associated.

Detection of outliers may be on one of the following basis:

(a) A known experimental aberration, such as an instrument failure or a technique inconsistency.

(b) A statistical test for significance, such as the Dixon ratio test. This test is described below.

The Dixon criteria is based entirely on ratios of differences between observations where it is desirable to avoid calculation of s or where quick judgment is called for. For the Dixon test, the sample criterion or statistic for various levels of significance are tabulated.

Table 14-1 presents selected significance (probability) levels for criteria over the n range 3 to 20. Note that the measurement values are first arranged in order of ascending magnitude: i.e., x_n is the largest value.

The ratios shown in Table 14-1 are used if the smallest value, x_1, is the suspected outlier. If the calculated value of the ratio is greater than the appropriate maximum ratio in the table, then x_i is declared an outlier. If the largest value, x_n, is the suspected outlier, then the appropriate ratios are shown below:

$n < 8$	$\frac{x_n - x_{n-1}}{x_n - x_1}$
$8 < n < 15$	$\frac{x_n - x_{n-2}}{x_n - x_2}$
$n \geq 15$	$\frac{x_n - x_{n-2}}{x_n - x_3}$

For this case, if the ratios calculated are greater than the appropriate maximum ratio shown in Table 14-1, then x_n is declared to be an outlier.

The control chart provides a tool for distinguishing the pattern of indeterminate (stable) variation from the determinate (assignable cause) variation. This technique displays the test data from a method in a form which graphically compares the variability of all test results with the average or expected variability of small groups of data - in effect, a graphical analysis of variance, and a comparison of the "within groups" variability versus the "between group" variability.

The data from a series of analytical trials can be plotted with the vertical scale in units of the test result and the horizontal scale in units of time or sequence of analyses. The average or mean value can be calculated and the spread (dispersion or range) can be established.

Table 14-1. MAXIMUM RATIO OF EXTREME RANKING OBSERVATIONS

Recommended for sample size	Rank difference ratio	Sample size, n	Maximum ratio Probability level 0.10	0.05	0.01
$n < 8$	$\frac{x_2 - x_1}{x_n - x_1}$	3	0.886	0.941	0.988
		4	0.679	0.765	0.889
		5	0.557	0.642	0.780
		6	0.482	0.560	0.698
		7	0.434	0.507	0.637
$8 < n < 15$	$\frac{x_3 - x_1}{x_{n-1} - x_1}$	8	0.650	0.710	0.829
		9	0.594	0.657	0.776
		10	0.551	0.612	0.726
		11	0.517	0.576	0.679
		12	0.490	0.546	0.642
		13	0.467	0.521	0.615
		14	0.448	0.501	0.593
$n \geq 15$	$\frac{x_3 - x_1}{x_{n-2} - x_1}$	15	0.472	0.525	0.616
		16	0.454	0.507	0.595
		17	0.438	0.490	0.577
		18	0.424	0.475	0.561
		19	0.412	0.462	0.547
		20	0.401	0.450	0.535

$x_1 < x_2 < x_3 \ldots < x_{n-2} < x_{n-1} < x_n$

14.6 CONTROL CHARTS

A. Application and Limitations

In order for quality control to provide a means for separating the determinate from indeterminate sources of variation, the analytical method must clearly emphasize those details which should be controlled to minimize variability. A check list includes:

1. Sampling procedures
2. Preservation of the sample
3. Aliquoting methods
4. Dilution techniques
5. Chemical or physical separations and purifications
6. Instrumental procedures
7. Calculation and reporting results.

The next step to be considered is the application of control charts for evaluations and control of these unit operations. Decisions relative to the basis for construction of a chart are required.

1. Choose method of measurement
2. Select the objective
   a. Precision or accuracy evaluation
   b. Observe test results, or the range of results
   c. Measurable quality characteristics
3. Select the variable to be measured (from the check list)
4. Basis of subgroup, if used:
   a. Size
      A minimum subgroup size of n=4 is frequently recommended. The change that small changes in the process average remain undetected decreases as the statistical sample size increases.
   b. Frequency of subgroup sampling
      Changes are detected more quickly as the sampling frequency is increased.

5. Control Limits

Control limits (CL) can be calculated, but judgment must be exercised in determining whether or not the value obtained satisfy criteria established for the method, i.e., does the deviation range fall within limits consistent with the solution or control of the problem. After the mean ($\bar{X}$) of the individual results (X) and the mean of the range ($\bar{R}$) of the replicate result differences (R) have been calculated, then CL can be calculated from data established for this purpose (Table 14-2).

Grand Mean ($\bar{\bar{X}}$) = X/k

CL's on Mean = $\bar{\bar{X}} \pm A_2$

Range ($\bar{R}$) = $\Sigma R/k$ or $d_{2\sigma}$

Upper Control Limit (UCL) on Range = $D_4\bar{R}$

Lower Control Limit (LCL) on Range = $D_3\bar{R}$

Where: k=number of subgroups, A_2, D_4 and D_3 are obtained from Table 4, R may be calculated directly from the data, or from the standard deviation (σ) using factor d_2. The lower control limit for R is zero when $n \leq 6$.

The calculated CL's include approximately the entire data under "in control" conditions, and therefore are equivalent to $\pm 3\sigma$ limits which are commonly used in place of the more laborious calculation. Warning lights (WL) set at $\pm 2\sigma$ limits (95%) of the normal distribution serve a very useful function in quality control. The upper warning limit (UWL) can be calculated by:

$$UWL = \bar{R} + 2\sigma_R$$

$$UWL = \bar{R} = 2/3 \quad D_4\bar{R}-\bar{R}$$

Table 14-2. FACTORS FOR COMPUTING CONTROL CHART LINES

Observations in subgroup (n)	Factor A_2	Factor d_2	Factor D_4	Factor D_3
2	1.88	1.13	3.27	0
3	1.02	1.69	2.58	0
4	0.73	2.06	2.28	0
5	0.58	2.33	2.12	0
6	0.48	2.53	2.00	0
7	0.42	2.70	1.92	0.08
8	0.37	2.85	1.86	0.14

Where the subgrouping is n = 2, UWL reduces to

$$UWL = 2.51\ \bar{R}.$$

B. Construction of Control Charts

1. Precision Control Charts

The use of range (R) in place of standard deviation (σ) is justified for limited sets of data $n \leq 10$ since R is approximately as efficient and is easier to calculate. The average range ($\bar{R}$) can be calculated from accumulated results, or from a known or selected σ ($d_2\sigma$). $LCL_R = 0$ when $n \leq 6$. (LCL = lower control limit.)

The steps employed in the construction of a precision control chart for an automatic analyzer illustrates the technique:

a) Calculate R for each set of side-by-side duplicate analyses of identical aliquots.

b) Calculate $\bar{R}$ from the sum of R value divided by the number (n) of sets of duplicates.

c) Calculate the upper control limit (UCL_R) for the range:

$$UCL_R = D_4\bar{R}$$

Since the analyses are in duplicates, $D_4 = 3.27$ (from Table 14-2).

d) Calculate the upper warning limit (UWL):

$$UWL_R = \bar{R} + 2\sigma_R = \bar{R} \pm 2/3\ (D_4\bar{R}) = 2.51\ \bar{R}$$

(D_4 from Table 1) which corresponds to the 95% confidence limits.

e) Chart $\bar{R}$, UWL_R and UCL_R on an appropriate scale which will permit addition of new results as obtained.

f) Plot results (R) and take action on out-of-control points.

2. Accuracy Control Charts -- Mean or Nominal Value Basis

$\bar{X}$ charts simplify and render more exact the calculation of CL since the distribution of data which conforms to the normal curve can be completely specific by $\bar{X}$ and σ. Stepwise construction of an accuracy

control chart for the automatic analyzer based on duplicate sets of results obtained from consecutive analysis if known serves as an example:

a) Calculate $\bar{X}$ for each duplicate set.

b) Group the $\bar{X}$ values into a consistent reference scale (in groups by orders of magnitude for the full range of known concentrations).

c) Calculate the UCL and lower control limit (LCL) by the equation.

$$CL = \pm A_2\bar{R} \quad (A_2 \text{ from Table 4})$$

d) Calculate the Warning Limit (WL) by the equation:

$$WL = \pm 2/3\ A_2\bar{R}$$

e) Chart CL's and WL's on each side of the standard which is set at zero as shown in Figure 12 and Table 6.

f) Plot the difference between the nominal value and $\bar{X}$ and take action on points which fall outside of the control limits.

14.7 PRECISION

This section provides the basis for the quantitative limits used to control the precision. Sections that follow address accuracy, and completeness of the data and the compliance with test procedures generated for this project. The primary measurement of data precision is the percentage Relative Standard Deviation, or the percentage Coefficient of Variation,

$$\%RSD \equiv \frac{s}{\bar{X}} \cdot 100, \text{ where}$$

the estimated standard deviation,

$$s = \sum_{i=1}^{n} \left[\frac{(X_i - \bar{X})^2}{n - 1} \right]^{\frac{1}{2}}, \text{ and}$$

the estimated mean,

$$\bar{X} \equiv \left[\sum_{i=1}^{n} \right] \frac{X_i}{n}.$$

Additional measures of precision will be calculated for the duplicate samples.

Where X_1 and X_2 are any measurement taken on duplicate samples 1 and 2,

$$\bar{x} = (X_1 + X_2)/2$$

$$s_x = \pm(X_1 - X_2)/\sqrt{2}$$

$$\% \text{ RSD} = \frac{s_x}{\bar{x}} \cdot 100 = \frac{100\sqrt{2}\ (X_1 - X_2)}{(X_1 + X_2)}$$

$$\%\text{RSD} = \frac{\sqrt{2}(X_1 - X_2)}{X_1 + X_2} \cdot 100$$

$$\%\text{RSD} = \frac{100\sqrt{2}\ (X_1 - X_2)}{(X_1 + X_2)}$$

14.8 ACCURACY

Accuracy is defined as the bias, or the difference between a measured value and an assumed true value. Thus,

$$B_i = X_i - T$$

or $$\%B_i = [(X_i - T)/T] \cdot 100.$$

For example, for any particular run using the GC/MS, one might calculate a bias, B_i or $\%B_i$, for the internal standard using the mean area as the expected or true value, T, by the equations given above. A better measure of accuracy will be given by the external standards that are expected to be used in the course of the project, considering the true values, T, to be those of the external standard.

14.9 COMPLETENESS

Measurement completeness, C, can be described as the ratio of acceptable measurements obtained to the total number of planned measurements for an item. In this program, the meaning of completeness has been extended to include supporting information such as identities, dates, or other data sheet entries. For this extended meaning, completeness is defined as:

$$C \equiv 1 - \frac{\text{number of defective items}}{\text{total number of items}}$$

The control criterion for completeness is based on a count of defective items within a time period sufficient to cause the total number of items to be large. A monthly count is used for this program.

15. CORRECTIVE ACTION

Corrective action procedures for this program will be initiated by the analyst directly involved with the laboratory procedures, by the laboratory supervisors or the QA coordinator specified in the program organization chart. Quality control charts of standard curves and intra-laboratory quality control samples will be utilized to indicate the necessity of corrective action. Control charts will be established for each procedure indicating upper and lower limits of 2 standard deviations as the acceptability ranges. At the point when the control charts show a deviation beyond the acceptability ranges, investigation as to the cause will be initiated. Corrective actions will also be initiated as a result of other QA activities which include performance audits, systems audits, and laboratory comparison studies.

The corrective action relative to the control charts relate more to precision than to accuracy. These charts give clues when some factor, generally of a procedural nature, is causing the results to drift or when an unexpected difference beyond the control limit occurs. The data within the upper and lower control limits of the control charts are well within the precision accuracy, and completeness criteria outlined in Section 5.5 above.

Corrective actions taken as a result of TRW internal audits will be initialed by a memorandum or an audit report and will be given to the program manager and to the party responsible for the action that needs correction. Part of the periodic audit procedure will be to verify that previously recommended corrective actions have been taken. Actions taken that do not result in the keeping the data within the goals set for precision, accuracy, and completeness will be reported to the EPA Project Officer and discussed with him.

16. QUALITY ASSURANCE REPORTS

The quality assurance officer will provide a written quality assurance report to the project manager on a monthly basis. This report will address quality control problems arising in the application of this QA plan, an assessment of the probable significances of the problems, and recommended actions. Quality control problems to be addressed may arise from:

- Poor compliance with test procedures reported by the several quality assurance monitors
- Completeness and precision test limit failures relayed through the quality assurance monitors
- In-Process procedure changes required by the nature of a specific sample matrix
- Quality control waivers dictated by operation conditions.

The assessment of the problem significance will be based, in part, on the probable effect on the program completeness and validity of inferences to be made from the data should the problem continue.

Recommended actions will include, as applicable:

- Tests which may clarify the problem, such as use of standards
- Corrective actions to alleviate the problem
- Further documentation of the problem
- Acceptance of the anomalous condition with associated risk

These reports will also include:

- Periodic assessment of measurement data accuracy, provision and completeness
- Results of performance and system audits.

The final report will contain a section summarizing the quality information contained in the monthly reports and for the entire project.

17. SAFETY CONSIDERATIONS

Personnel from Radian will adhere to all the General Safety Rules as specified in its internal safety documents as well as all the safety rules specified by CE Raymond at this test facility. In addition to these general safety specifications, the Radian test personnel will be equipped with respiratory protection specific for the removal of cyanide. The test personnel responsible for the mixing of the cyanide will be protected from accidental spills and splashes by protective clothing and face shields.

Two portable cyanide monitors are to be purchased for this project with audible alarms set to an ambient air concentration of 10 ppm or greater of NaCN or HCN. These monitors will be placed in the areas most susceptible to problems such as the mixing area, the kiln/afterburner and the instrument analysis area.

A continuous monitor will be purchased for the analysis of the stack gases and will monitor in the 0-100 ppm range. If for any reason the stack gases exceed 10 ppm HCN in the exhaust gases, the test will be terminated.

18. REFERENCES

1. Personal conversation between Joe Furgo and Don Oberacker.

APPENDIX

Cyanide (as CN)

Analyte:	Cyanide	Method No.:	S250
Matrix:	Air	Range:	2.6-9.7 mg/cu m
OSHA Standard:	5 mg/cu m	Precision ($\overline{CV}_T$):	0.103
Procedure:	Collection with filter and impinger, Extraction with 0.1N NaOH, ion specific electrode	Validation Date:	1/30/76

1. Principle of the Method

1.1 Atmospheric samples are collected by drawing a known volume of air through a cellulose membrane filter and impinger (connected in series) containing 0.1N sodium hydroxide.

1.2 The sample-containing filters are extracted with 0.1N sodium hydroxide.

1.3 The filters and impingers are analyzed separately by direct potentiometry using an ion specific electrode.

1.4 The millivolt reading is used as a measure of cyanide concentration based on a calibration curve generated by measurement of standard solutions.

1.5 The samples must be carefully interspersed between calibration standards which give about the same response as the samples in order to obtain reliable results.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.62-9.68 mg/cu m at an atmospheric temperature and pressure of 24°C and 763 mm Hg, using a 90-liter sample. Under the conditions of sample size (90 liters), the linear working range of the method is estimated to be 0.5-15 mg/cu m.

90L sample gas

2.2 The lower limit of detection for cyanide is noted as 0.1 µg/ml.

3. Interferences

3.1 Gaseous hydrogen cyanide present in the air is an interference.

3.2 Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if found to be present in the sample. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

3.3 Sulfide is removed by the addition of a small amount (spatula tip) of powdered cadmium carbonate to the pH 11-13 sample. Swirl to disperse the solid and recheck the liquid by again touching a drop to a piece of lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution.

3.4 When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool contained in an eye dropper and proceed with the analysis.

3.5 It should also be noted that the cyanide electrode will malfunction if other ions like chloride, iodide and bromide, which form insoluble silver salts are present in sufficient quantity. Several metal ions are also known to complex with cyanide, such as cadmium, zinc, silver, nickel, cuprous, iron, and mercury. Consult the instruction manual for a list of these ions and also the proper procedure to use when such ions are believed to be present.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2.62-9.68 mg/cu m was 0.101. This value corresponds to a 0.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 A collection efficiency of 100% was determined for dry particulate cyanide on the cellulose membrane filter and a collection efficiency of 98% was determined for HCN in 0.1N NaOH; thus, no bias was introduced in the sample collection step based on collection efficiency. Likewise, data on a limited number of analytical filter samples give an average recovery of 97%. In the absence of a significant amount of "free" HCN in the environment being sampled, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

Advantages are the simplicity, specificity, and speed of the method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal samples for the determination of cyanide content consists of the following components.

6.1.1 A filter unit which consists of the filter media (Section 6.2) and 37-mm, 3-piece cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate. The pump must be calibrated with a filter and impinger in the line.

6.1.4 Thermometer

6.1.5 Manometer

6.1.6 Stopwatch

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8 micrometer pore size.

6.3 Polyethylene scintillation vials with screw caps, 20 ml.

6.4 Orion 94-06 Cyanide ion specific electrode or equivalent.

6.5 Orion 90-20-00 double junction reference electrode or equivalent.

6.6 A pH meter with readout capacity in increments of 0.1 millivolt.

6.7 Magnetic Stirrer and Stirring Bars.

6.8 Jars for extraction of filters: 2 oz. ointment jars, squat form with aluminum-lined screw caps.

6.9 Pipets, 10 ml and other convenient sizes.

6.10 Volumetric flasks, 25 ml and other assorted sizes.

6.11 Associated laboratory glassware.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 Double distilled water

7.2 Potassium Cyanide

7.3 Sodium Hydroxide 0.1N. Dissolve 2.0 g NaOH in double distilled water and dilute to 500 ml.

7.4 Cyanide Standards

7.4.1 Cyanide Standard Stock solution, 200 µg/ml. Dissolve 0.50 g KCN in 0.1N NaOH and dilute to 1000 ml with additional 0.1N NaOH.

7.4.2 Working standards. Prepare at least 6 working standards to cover the concentration range of interest by proper dilution of the stock standard to a total volume of 25 ml. Use 0.1N NaOH for all dilutions. Prepare these calibration standards fresh daily.

7.5 Lead Acetate Paper

7.6 Cadmium Carbonate

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use all glassware should initially be soaked in a strong detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, the glassware should be thoroughly rinsed with warm tap water, concentrated nitric acid, tap water, and distilled water, in that order, and then dried.

8.2 Calibration of Personal Pump. Personal sampling pump should be calibrated using integrating volume meter (6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 To collect cyanide salts, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1) connected in series to a midget impinger containing 10 ml of 0.1N NaOH.

8.3.2 The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter.

8.3.3 A short piece of flexible tubing is used to connect the filter holder to the impinger. A similar piece of flexible tubing, loosely plugged with a piece of glass wool to protect the sampling pump from splashover and condensation, is used to connect the impinger to the sampling pump. The impinger must be maintained in a vertical position during the sampling. Clip the cassette to the worker's lapel.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.5 Set the flow rate as accurately as possible using the manufacturer's directions. Record the temperature and

pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Position the middle of the rotameter ball of the personal sampling pump to the 1.5 liter per minute calibration mark as accurately as possible. Since it is possible for the filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and readjusted as needed. If the rotameter cannot be adjusted to correct a problem, terminate the sampling.

8.3.6 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1.5 liters per minute for 60 minutes (90 liters).

8.3.7 After sampling disconnect the filter holder cassettes from the impingers and firmly seal the cassettes with the plugs in both the inlet and outlet.

8.3.8 The sample impingers are then handled and shipped separately from the filters. The impinger stems can be removed and cleaned as follows. Tap the stem gently against the inside wall of the impinger bottom to recover as much of the sampling solution as possible and quantitatively transfer the total contents of the impinger bottom into a 20-ml polyethylene scintillation vial with screw cap. Wash the impinger stem with 2 ml of 0.1N NaOH and add washing into the polyethylene vial. Close cap tightly and secure with plastic tape around edges to avoid sample loss during transit.

8.3.9 Care should be taken to minimize spillage or loss by evaporation at all times.

8.3.10 Carefully record sample identity of both filters and impingers and all relevant sample data.

8.3.11 Blank. With each batch of 10 samples, submit one filter and one impinger solution which is subjected to exactly the same handling as for the samples except that no air is drawn through them. Label these as blanks. Submit one blank filter and one blank impinger solution for every ten samples.

8.4 Analysis of Samples

8.4.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers and transfer filter to a 2 oz. ointment jar.

8.4.2 Pipet 25 ml of 0.1N NaOH into the jar. Cap and allow to stand for at least 30 minutes with occasional shaking. Tests indicate that this period is adequate for complete extraction of the cyanide from the filter. Analyze these filter samples within 2 hours after extraction.

8.4.3 The impinger sample solutions contained in the polyethylene vials are also made up to a 25-ml volume.

8.4.4 Potentiometric Measurements.

1. The samples are analyzed by immersing the cyanide ion electrode and reference electrode in the sample solutions and recording the millivolt reading. Both the samples and standards should be stirred while the readings are being taken. The reading should be taken after the meter has stabilized. Follow instrument manufacturer's instruction manual for proper operation and measurement procedures.

2. To obtain the most reliable results, the samples should be carefully interspersed with standards of similar response.

8.4.5 Appropriate filter blanks and impinger blanks must be analyzed by the same procedure used for the samples.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method for particulate cyanide, it is necessary to determine the recovery of the analyte. The analyte recovery should be determined in duplicate for at least one concentration which corresponds to a weighable amount. If the recovery of the analyte is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A weighed amount of the analyte, preferably equivalent to the concentration expected in the sample, is added to a representative cellulose membrane filter. The analyte is then recovered from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level has been used for the recovery studies. Six filters were spiked with weighed amounts of potassium cyanide equivalent to the CN present at 2X OSHA standard level. A parallel blank filter was also treated in the same manner except that no analyte was added to it. All

filters were then analyzed as described in Section 8.4. The average recovery value obtained was found to be 97%.

The recovery equals the average weight in µg recovered from the filter divided by the weight in µg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (µg) Recovered}}{\text{Weight (µg) Added}}$$

9. Calibration and Standards

9.1 Prepare a series of working standards containing 40-1000 micrograms of cyanide in 25 ml of 0.1N sodium hydroxide. These standards should be prepared fresh each time. Refer to Section 7.4. It is convenient to express concentration of standards in terms of µg per 25 ml, because samples are in this volume of solvent.

9.2 The appropriate calibration standards are alternately analyzed with the samples to determine the response factor. This practice will minimize the effect of observed fluctuations or variations in millivolt readings during any given day.

9.3 On semilog paper, plot the millivolt readings vs. cyanide ion concentrations of the standards. The cyanide ion concentration in µg/25 ml is plotted on the log axis.

10. Calculations

10.1 Determine the weight in micrograms corresponding to the millivolt response of the sample by using the appropriate response factor or calibration factor for the sample.

10.2 Separately calculate the amount of particulate cyanide found on the filter and the cyanide (HCN) found in the impinger.

10.3 Corrections for the blank must be made for each sample filter and impinger.

$$\text{µg} = \text{µg sample} - \text{µg blank}$$

where:

µg sample = µg found in sample filter or sample impinger
µg blank = µg found in blank filter or blank impinger

10.4 Divide the total weight of CN from filter by the recovery to obtain the corrected µg/sample.

$$\text{Corrected µg/sample} = \frac{\text{Total Weight}}{\text{Recovery}}$$

10.5 Report the particulate cyanide found and the HCN found as separate values because the OSHA standards for these two species are different. Note that the HCN found may be due to free HCN as well as HCN formed from moisture interaction with the particulate CN during sampling.

10.6 If HCN is known to be absent in the environment being sampled, then the sum of the CN found on the filter and the impinger solution gives a total measure of particulate cyanide.

10.7 If air samples were taken under conditions significantly different from standard conditions of 25°C and 760 mm Hg, a volume correction for the air sampled should be made as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters @ 25°C and 760 mm Hg
V = volume of air sampled
P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

10.8 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected µg (Section 10.4)}}{\text{Air Volume Sampled (Liter)}}$$

11. References

11.1 Instruction Manual for cyanide ion specific electrode.

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

CYANIDE IN AIR

Physical and Chemical Analysis Branch
Analytical Method

Analyte:	Cyanide	Method No.	P&CAM 116
Matrix:	Air	Range:	0.013 -13 mg/m³
Procedure:	Collection via Impinger/ Ion Specific Electrode		
Date Issued:	9/8/72	Precision:	Unknown
Date Revised:	12/1/73	Classification:	D (Operational)

1. Principle of the Method

   1.1 Atmospheric samples are taken using midget impingers that contain 10 mℓ of 0.1M NaOH.

   1.2 Samples are analyzed using the cyanide ion specific electrode.

2. Range and Sensitivity

   The range and sensitivity of the method have not been established at this time. The recommended range of the method is 0.013-13 mg/m³ in air.

3. Interferences

   3.1 Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if found to be present in the sample. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

   3.2 Sulfide is removed by the addition of a small amount (spatula tip) of powdered cadmium carbonate to the pH 11-13 sample. Swirl to disperse the solid, and recheck the liquid by again touching a drop to a piece of lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution.

3.3 When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool contained in an eye dropper and proceed with the analysis.

4. Precision and Accuracy

The precision and accuracy of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

5. Advantages and Disadvantages of the Method

Advantages are the simplicity, specificity, speed and accuracy of the method.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 Orion 94-06 Cyanide ion specific electrode or equivalent.
6.3 Orion 90-01 Single junction reference electrode or equivalent.
6.4 Expanded scale millivolt – pH meter.
6.5 Associated Laboratory Glassware.
6.6 Plastic Bottles.
6.7 Magnetic Stirrer and Stirring Bars.

7. **Reagents**

The reagents described must be made up using ACS reagent grade or better grade of chemical.

7.1 Double distilled water.

7.2 Potassium Cyanide.

7.3 Sodium Hydroxide 0.1M. Dissolve 2.0 g NaOH in double distilled water and dilute to 500 mℓ.

7.4 Potassium Cyanide Standards

7.4.1 Dissolve 0.65 g KCN in 0.1M NaOH and dilute to 100 mℓ with additional 0.1M NaOH for 10^{-1} M[CN^-] (2600 μg/mℓ).

7.4.2 Dilute 10 mℓ of 10^{-1} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-2} M[CN^-] (260 μg/mℓ).

7.4.3 Dilute 10 mℓ of 10^{-2} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-3} M[CN^-] (26 μg/mℓ).

7.4.4 Dilute 10 mℓ of 10^{-3} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-4} M[CN^-] (2.6 μg/mℓ).

7.4.5 Dilute 10 mℓ of 10^{-4} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-5} M[CN^-] (0.26 μg/mℓ).

7.5 Lead Acetate Paper.

7.6 Cadmium Carbonate

8. **Procedure**

8.1 Cleaning of Equipment. All glassware is washed in detergent solution, rinsed in tap water and then rinsed with double distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Pour 10 mℓ of the absorbing solution (Section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 2.5 ℓ pm. A sample size of not more than 200 liters and no less than 10 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 0.5 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 Analysis of Samples

8.3.1 The solution is quantitatively transferred from the impinger to a 50-cc beaker.

8.3.2 The cyanide ion electrode and the single junction reference electrode are placed in the solution and the resulting millivolt reading recorded. The reading should be taken after the meter has stabilized. Both the samples and standards should be stirred while the readings are being taken.

9. Calibration and Standards

9.1 Obtain the millivolt readings from each of the cyanide standards.

9.2 Plot the millivolt readings vs. the cyanide ion concentrations of the standards on semi-log paper. The cyanide ion concentration in $\mu g/m\ell$ is plotted on the log axis.

10. Calculations

10.1 The millivolt readings from the analysis of the sample are converted to $\mu gCN/m\ell$ of solution using the calibration curve.

10.2 The μg content of the sample is multipled by the sample volume to obtain the total μgCN in the sample.

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = Barometric Pressure in mm Hg
T = Temperature of air in degree centrigrade.

10.4 The concentration of CN in the air sampled can be expressed in μg CN per liter or mg CN per cubic meter.

$mg/m^3 = \mu g/liter$

$$mg/m^3 = \frac{\text{total } \mu g \text{ CN}}{V_s}$$ (Section 10.2) / (Section 10.3)

10.5 The concentration of CN can also be expressed in ppm, defined as μℓ of component per liter of air.

$$\text{ppm} = \mu\ell\ \text{CN}/V_s = R/MW\ \mu g\ \text{CN}/V_s$$

$$= 0.94 \times \mu g\ \text{CN}/V_s$$

where:

$R = 24.45$ at 25°C, 760 mm Hg.
$MW = 26$

11. References

11.1 Cyanide Ion Specifications, Orion Research, Inc., Cambridge, MA.

11.2 Frant, M.S., "Detecting Pollutants with Chemical Sensing Electrodes," Environ. Sci. Tech., 8, 224 (1974).

EPA-625-/6-74-003a

METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
Environmental Research Center
Cincinnati, Ohio 45268

U.S. ENVIRONMENTAL PROTECTION AGENCY
Technology Transfer

1976

TABLE 2

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT (1)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time(6)
Acidity	100	P, G[2]	Cool, 4°C	24 Hrs.
Alkalinity	100	P, G	Cool, 4°C	24 Hrs.
Arsenic	100	P, G	HNO_3 to pH <2	6 Mos.
BOD	1000	P, G	Cool, 4°C	6 Hrs.[3]
Bromide	100	P, G	Cool, 4°C	24 Hrs.
COD	50	P, G	H_2SO_4 to pH <2	7 Days
Chloride	50	P, G	None Req.	7 Days
Chlorine Req.	50	P, G	Det. on site	No Holding
Color	50	P, G	Cool, 4°C	24 Hrs.
Cyanides	500	P, G	Cool, 4°C NaOH to pH 12	24 Hrs.
Dissolved Oxygen				
Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	4-8 Hours

CYANIDE, Total
in water

STORET NO. 00720

1. Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface, and saline waters, domestic and industrial wastes.

(1) 1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.2 mg/200 ml of absorbing liquid).

(2) 1.3 The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 0.02 mg/l.

2. Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of cuprous ion.

4. Sample Handling and Preservation

4.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

4.2 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample ($pH \geq 12$) at the time of collection.

4.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

4.4 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

5. Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure (8.1 through 8.5).

5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the sample on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the stabilized sample (pH≥12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1+9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

6. Apparatus

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling

flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

7. Reagents

7.1 Sodium hydroxide solution: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: powdered.

7.3 Ascorbic acid: crystals.

7.4 Cuprous Chloride Reagent: Weigh 20 g of finely powdered Cu_2Cl_2 into an 800 ml beaker. Wash twice, by decantation, with 250 ml portions of dilute sulfuric acid (H_2SO_4, 1 + 49) and then twice with water. Add about 250 ml of water and then hydrochloric acid (HCl, sp gr 1.19) "cautiously" until the salt dissolves (See Note 1). Dilute to 1 liter with distilled water and store in a tightly stoppered bottle containing a few lengths of pure copper wire or rod extending from the bottom to the mouth of the bottle (See Note 2).

Note 1: Approximately 100 ml of HCl will be required for dissolution. The reagent should be clear; dark discoloration indicates the presence of cupric salts.

Note 2: If it is desired to use a reagent bottle of smaller volume, it should be kept completely filled and tightly stoppered. Refill it from the stock solution after each use.

7.5 Sulfuric acid: concentrated.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 ml = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 10.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 10μg).

7.9 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 1.0μg CN (1.0 mg/l).

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 ml (1 ml = mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color Reagent – One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark plate.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution. Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1,1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

8. Procedure

8.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Slowly add 25 ml conc. sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 10 ml of Cu_2Cl_2 reagent (7.4) into the air inlet and wash down with a stream of water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.5 Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.6 Withdraw 50 ml of the solution from the volumetric flask and transfer to a 100 ml volumetric flask. Add 15 ml of sodium phosphate solution (7.6) and 2.0 ml of Chloramine T solution (7.12) and mix. Immediately add 5.0 ml pyridine-barbituric acid solution (7.13.1), or pyridine-pyrazolone solution (7.13.2.3), mix and bring to mark with distilled water and mix again.

NOTE: If 2 ml chloramine T solution produces a precipitate with pyridine-pyrazolone, use a lesser amount (0.2 ml) making certain that an excess of chlorine is present.

8.7 For pyridine-pyrazolone solution allow 40 minutes for color development then read absorbance at 620 nm in a 1 cm cell. When using pyridine-barbituric acid, allow 8 minutes for color development then read absorbance at 578 nm in a 1.0 cm cell within 15 minutes.

8.8 Prepare a series of standards by diluting suitable volumes of standard solution to 500.0 ml with distilled water as follows:

ml of Standard Solution (1.0 = 1μg CN)	Conc., When Diluted to 500 ml, mg/1 CN
0 (Blank)	0
5.0	0.01
10.0	0.02
20.0	0.04
50.0	0.10
100.0	0.20
150.0	0.30
200.0	0.40

8.8.1 Standards must be treated in the same manner as the samples, as outlined in (8.1) through (8.7) above.

8.8.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.3 Subsequently, at least two standards (a high and a low) should be treated as in (8.8.1) to verify standard curve. If results are not comparable (±20%), a complete new standard curve must be prepared.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to insure a level of 20μg/1 or a significant increase in absorbance value. Proceed with the analysis as in Procedure (8.8.1) using the same flask and system from which the previous sample was just distilled.

8.9 Alternatively, if the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.

8.10 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.11 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.

9. Calculation

9.1 Using the colorimetric procedure, calculate concentration of CN, mg/l, directly from prepared standard curve compensating for sample dilution if less than 500 ml was used for distillation.

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(A-B)\ 1000}{\text{ml original sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of $AgNO_3$ for titration of sample.

B = volume of $AgNO_3$ for titration of blank.

10. Precision and Accuracy

10.1 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN, the standard deviations were ±0.005, ±0.007, ±0.031, and ±0.094, respectively.

10.2 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85% and 102%, respectively.

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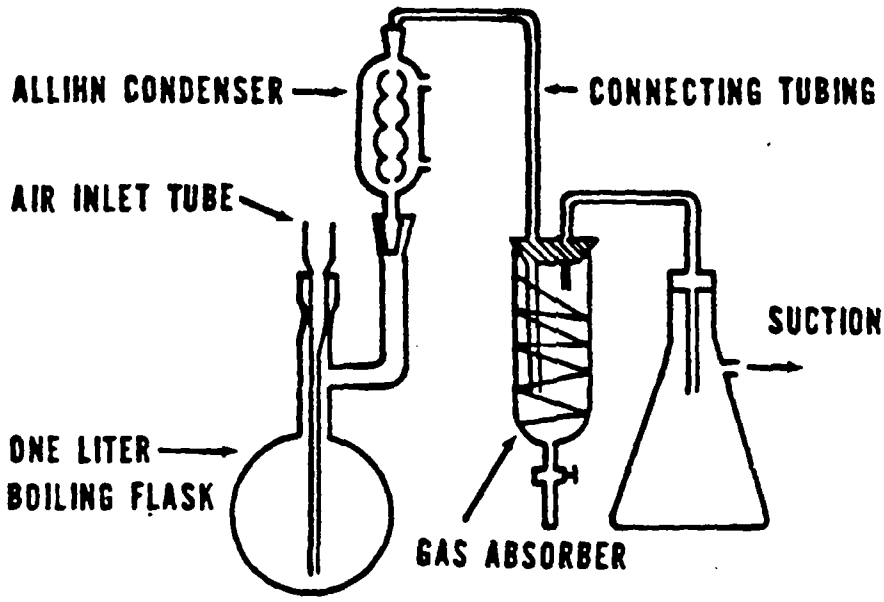

FIGURE 1

CYANIDE DISTILLATION APPARATUS

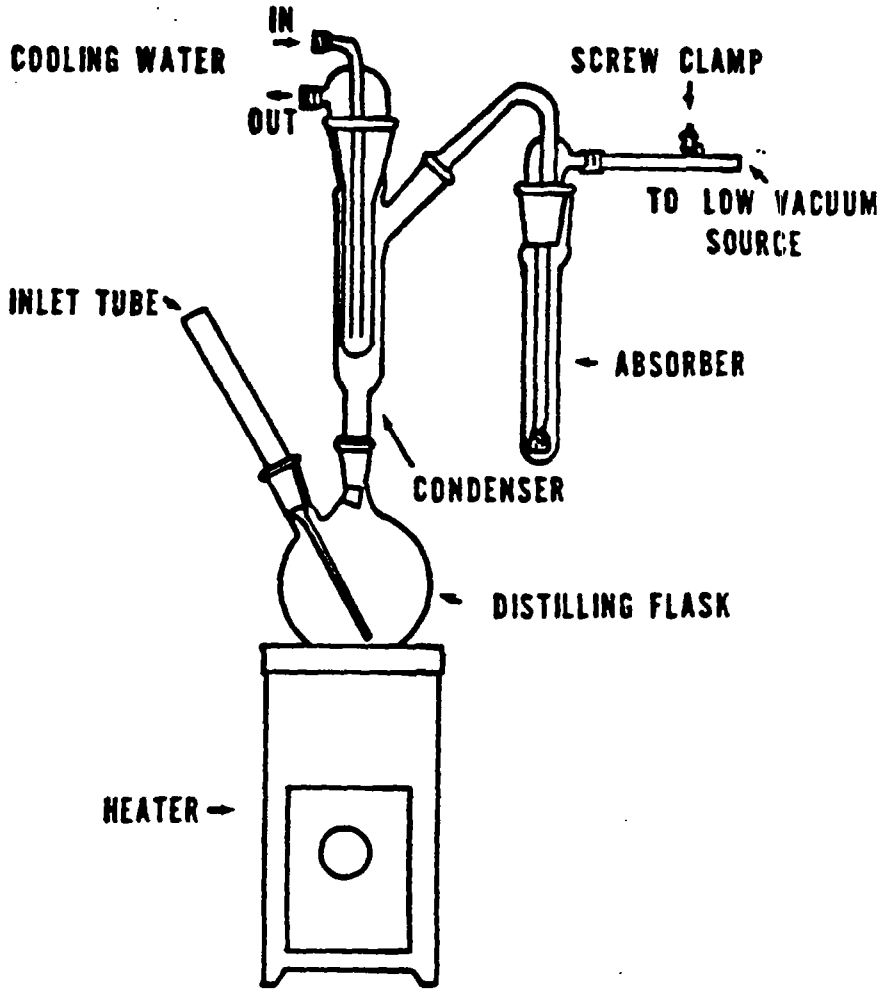

FIGURE 2

CYANIDE DISTILLATION APPARATUS

CYANIDES, Amenable to Chlorination

STORET NO. 00722

1. Scope and Application

1.1 This method is applicable to the determination of cyanides amenable to chlorination in drinking, surface, and saline waters, and domestic and industrial wastes.

1.2 The titration procedure is used for measuring concentrations of cyanide exceeding 1 mg/l after removal of the cyanides amenable to chlorination. Below this level the colorimetric determination is used.

2. Summary of Method

2.1 A portion of the sample is chlorinated at a pH>11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Cyanide, Total, in this manual. Cyanides amenable to chlorination are then calculated by difference.

3. Reagents

3.1 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 ml of distilled water.

3.2 Sodium Hydroxide solution: Dissolve 50 g of sodium hydroxide (NaOH) in distilled water and dilute to 1 liter.

3.3 Ascorbic acid: crystals.

3.4 Potassium Iodide - starch test paper.

4. Procedure

4.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 ml aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution (3.1) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (3.2).

Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.

4.2 Test for residual chlorine with KI-starch paper (3.4) and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

4.3 After one hour, add 0.5 g portions of ascorbic acid (3.3) until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to insure the presence of excess reducing agent.

4.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots as in the method Cyanide, Total, in this manual.

5. Calculation

5.1 Calculate the cyanide amenable to chlorination as follows:

CN, mg/l = A−B

where:

A = mg/l total cyanide in unchlorinated aliquot

B = mg/l total in chlorinated aliquot

Bibliography

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A.P.S. 1000 M 1200 m'
45.26 IVH4S2O8 54.31
3.42 AgNO3 4.10

DECEMBER 1978

EMISSIONS ASSESSMENT OF CONVENTIONAL STATIONARY COMBUSTION SYSTEMS

METHOD AND PROCEEDURES MANUAL FOR SAMPLING AND ANALYSIS

FINAL REVISION SUPERCEDING DRAFTS
OF JANUARY AND SEPTEMBER, 1977

BY

J. W. Homersma, D. G. Ackerman, M. M. Yamada, C. A. Zee, C. Y. Ung, K. T. McGregor, J. F. Clausen, M. L. Kraft, J. S. Shipiro, and E. L. Moore

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6.5.11 Cyanide, Free

6.5.11.1 Scope and Application

This method is applicable to the determination of free cyanide in saline and non-saline waters, domestic and industrial wastes. If a total cyanide concentration value is required, i.e., a value for both free and complex cyanides, a distillation must be performed prior to analysis.[1]

6.5.11.2 Summary of Method

Free cyanide is determined colorimetrically using the prepackaged Hach Model CYN-2 Cyanide Test Kit. Although the contents of the "Powder Pillows" used in the reaction are not stated, it is quite probable that as in the standard colorimetric measurement procedure the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine -T at a pH less than 8. When this reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The color intensity is then compared with standard colors to determine the free cyanide content of the sample.

6.5.11.3 Interferences

Although the Hach procedure[2] does not discuss interferences, it is most probable that sulfides would adversely affect this procedure, as well as the standard colorimetric technique.

If a drop of sample on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the stabilized sample (pH≥12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

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[1]Distillation procedure may be found in ASTM Standards, Part 23, Water: Atmospheric Analyses, p. 498, Method D2036-72 Reference Method A(p 173).

[2]Hach Direct Reading Engineers Laboratory Methods Manual (DR-EL/2).

6.5.11.4 Sample Handling and Preservation

Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

If a sample were to be returned to the laboratory for subsequent distillation and total cyanide analysis, the sample should be collected in plastic bottles of 1 liter or larger size. (All bottles must be throughly cleansed and thoroughly rinsed to remove soluble material from containers.) The sample must also be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH≥12) at the time of collection.

6.5.11.5 Apparatus

- Hach Portable Test Kit Spectrophotometer
- Standard laboratory glassware.

6.5.11.6 Reagents

Reagents for the Hach Model C4N-2 Cyanide Test Kit include the following:

1) Metal Inhibitor Powder Pillow
2) CyaniVer I Powder Pillow
3) CyaniVer II Powder Pillow

6.5.11.7 Procedure

1) If the water sample is turbid, filter a sample for testing. To do this, place the funnel on one of the square mixing bottles. Place a piece of folded filter paper in the funnel. Pour the water sample into the filter paper and allow it to pass through. Filter enough sample to fill the square mixing bottle up to the shoulder.
2) Add the contents of one Metal Inhibitor Powder Pillow to the filtered sample. Swirl to mix.
3) Add the contents of one CyaniVer I Powder Pillow. Swirl to mix and dissolve.
4) Add the contents of one CyaniVer II Powder Pillow. Swirl to mix and dissolve. If cyanide is present, a pink color will develop in a short time. Allow 15 minutes for color development, during which the color becomes progressively more purple,

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